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FABRICATION AND EVALUATION OF NEW RESINS

M. G. Maximovich
S. Lockerby
J. F. Wolfe

SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

June 1979

Interim Report April 1978-April 1979

Air Force Materials Laboratory
Air Force Wright Aeronautical Laboratories
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

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This technical report has been reviewed and is approved for publication.

F. E. ARNOLD
Project Monitor

R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

FOR THE COMMANDER

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Polyimide films, RPS, enyne polysulfones, IMC polymers, graphite reinforced composites, rodlike aromatic heterocyclic polymers, PBT, condensation polymerization.

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Films were fabricated from a variety of polyimide with six member and five member imide rings, various mixes of RPS reactive plasticizer and P1700 polysulfone were evaluated and compared as matrix resins for graphite reinforced composites, IMC polymers (enyne-polysulfones) were evaluated and compared to unmodified polymers.

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20. (Abstract)

The rodlike aromatic heterocyclic polymer, PBT, was prepared by a batch process in PPA. The resultant polymers showed very high intrinsic viscosities. PBT is a candidate for use as a high modulus/high strength structural material.

FOREWORD

This interim report presents the continuation of the work reported in interim reports AFML-TR-77-59 and AFML-TR-78-32. These results were obtained during the past 12 months on a study dealing with the fabrication and evaluation of new resins for the Air Force Materials Laboratory, Wright-Patterson Air Force Base, under Contract F33615-76-C-5109, Project 2419, "New Polymers to Provide the Basis for Nonmetallic Materials for Aircraft and Missile Structures." This work was administered under the direction of Dr. F. E. Arnold (AFML/MBP), Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio.

This report covers work performed from 6 April 1978 to 6 April 1979 and was prepared by M. G. Maximovich, S. Lockerby and J. F. Wolfe. The assistance of O. Bergren in prepreg and composite fabrication and testing, of B. Loo in synthesis of ordered polymers, and of G. Peirce and V. Simmon in conducting mutagenicity studies is gratefully acknowledged.

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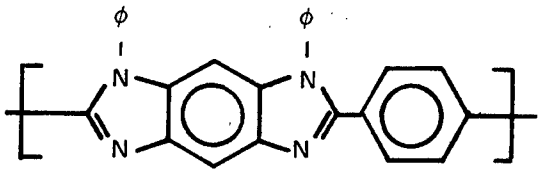
I INTRODUCTION

The intrinsic property of fully chain-extended polymers to form anisotropic or ordered solutions provides the basis for a program of new materials research sponsored by the United States Air Force. The objective of the Ordered Polymer Program is to demonstrate that structural forms with superior mechanical properties can be obtained from these ordered solutions. The unique feature of this program is that candidate polymers have been limited to those composed entirely of aromatic and aromatic heterocyclic units in order to achieve the maximum use-temperature from an organic material.

There are a limited number of possible molecular structures that are simultaneously rodlike, aromatic, soluble to the extent that they form anisotropic solutions, and attainable by a suitable polycondensation reaction in greater than 99.5 percent yield. The objective of the present work, therefore, was to screen a number of candidate systems for synthetic feasibility and to provide a preliminary characterization of promising systems. In our last annual[1] report we described efforts to synthesize four polymer systems with the requisite rodlike structure. These structures are shown in Figure 1.

The diphenyl benzobisimidazole polymer 1 was reported by Korshak[2] to form by a two step process via a poly(o-anilinoamide). We found that ring closure of this prepolymer gave relatively low viscosity materials without the reported solubility in organic solvents. The requisite monomer for the isomeric benzobisimidazole 2, namely N^1,N^4-diphenyl-1,2,4,5-tetraaminobenzene, could not be prepared due to the undesired substitution of nitro groups by aniline in the dichloro-p-dinitrobenzene precursors. The monomer necessary for the preparation of the benzobisthiazole polymer 3, namely, 1,3-diamino-4,6-benzenedithiol dihydrochloride 5, was reported by Marvel[3] to be unstable resulting in a material of unreliable purity. We concurred with this observation when we obtained low yields of the desired product in reactions of the monomer 5 with benzoic acid in polyphosphoric acid (PPA) and obtained low molecular weight polymers from the reaction of 5 with terephthalic acid in PPA.

The synthesis of the benzobithiazole polymer 4, however, met with considerable success. We prepared the new monomer, 1,4-diamino-2,5-benzenedithiol dihydrochloride (6), in fair yield and good purity by the route shown in Figure 2. The reaction of 6 with benzoic acid in polyphosphoric acid (PPA) gave the model compound 2,6-diphenylbenzo(1,2-d:4,5-d')bisthiazole (7) in 98.9 percent isolated yield.



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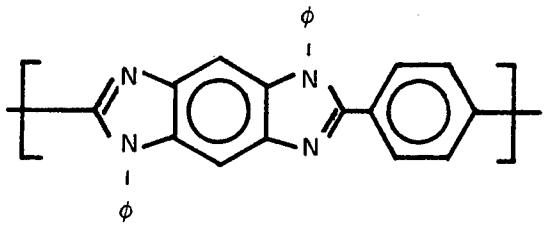

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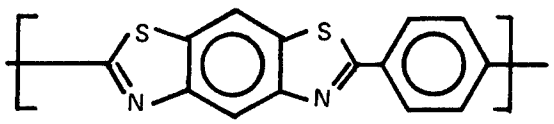

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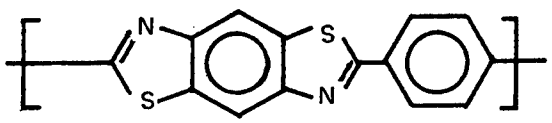

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Figure 1 Rodlike Aromatic Heterocyclic Polymers (1-4)

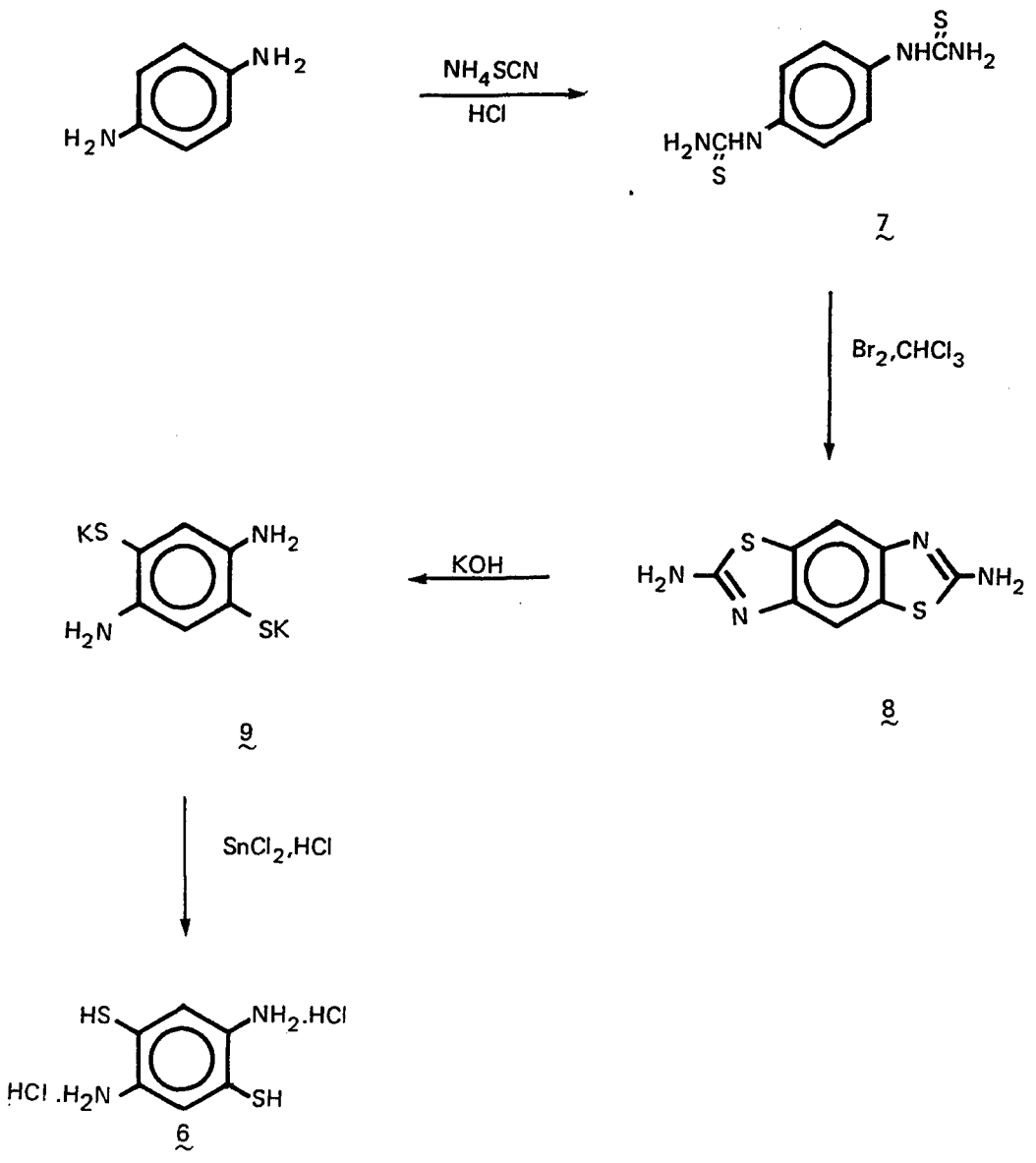
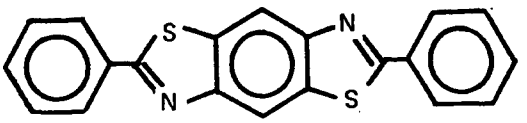


Figure 2 Synthesis of 1,4-Diamino-2,5-Benzenedithiol Dihydrochloride



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Two polycondensations of 6 with terephthalic acid in PPA afforded polymers in quantitative yield with intrinsic viscosities of 5 and 9 dl/g (MSA, 30°C). Polymer 4, or PBT, showed excellent thermooxidative stability and solution behavior.

The objective of the current work was to improve the yield and techniques used in the PBT monomer synthesis and to optimize PBT polymerization parameters. Additional characterization of the model compound was performed. The standard Ames salmonella/microsome test for mutagenicity was conducted on the monomers used for the preparation of PBO and PBT and on a PBT monomer precursor.

II SUMMARY

A. Synthesis of 1,4-Diamino-2,5-benzenedithiol dihydrochloride (6)

The synthesis of the PBT monomer 6 was performed essentially as reported in our last annual report; as outlined in Figure 2. A method for the large scale purification of p-phenylenediamine was employed to give uniform purity of the bisthiourea. Three recrystallizations from acetic acid were necessary to obtain diaminobenzobisthiazole intermediate of sufficient purity. Three recrystallizations and careful drying were determined to be the critical factors in obtaining monomer 6 of the required purity.

B. PBT Synthesis

Modifications on the reported procedure[1] for the preparation of PBT afforded material with intrinsic viscosities as high as 15.6 dl/g. A systematic study of the reaction parameters necessary for preparation of PBT with optimum molecular weight was beyond the scope of this program and the development of PBT under this contract was discontinued. It should be noted that 200 g of PBT was prepared at SRI under a separate Air Force contract according to the conditions determined under this contract. Intrinsic viscosities of 14 and 18 dl/g were obtained. Development of PBT has been continued under a separate Air Force contract at SRI and viscosities as high as 26 dl/g in MSA have been obtained.

C. Mutagenicity Studies on PBO Monomer, PBT Monomer, and a PBT Monomer Precursor

Due to the increased possibility of exposure of workers to these new compounds, we felt it necessary to conduct a preliminary study on their possible carcinogenicity. From the results given in this report, we concluded that 2,6-diaminobenzo[1,2-d:4,5-d']bisthiazole and the PBT monomer, 2,5-diamino-1,4-benzenedithiol dihydrochloride, were not mutagenic in the standard Ames Salmonella/microsome test. The PBO-monomer, 4,6-diaminoresorcinol dihydrochloride, was weakly mutagenic to two of the strains tested.

D. Attempted Polymerization of 4,6-Diaminoresorcinol Dihydrochloride with Terephthalic Acid

The preparation of the oxygen analog of PBT was attempted using the above monomers under the same conditions as those used for PBT. A black, nonpolymeric material was obtained. We concluded that the diaminodiol monomer was not stable under the reaction conditions employed.

III TECHNICAL DISCUSSION

A. Synthesis of 1,4-Diamino-2,5-benzenedithiol Dihydrochloride (6)

The PBT-forming monomer, 2,5-diamino-1,4-benzenedithiol (6), was synthesized by the scheme shown in Figure 2.

A mixture of one mole of p-phenylenediamine, 2.5M hydrochloric acid, and activated charcoal was filtered to give a clear yellow solution. Four moles of ammonium thiocyanate and additional concentrated hydrochloric acid were added and the solution was heated at the reflux temperature for 18 hrs. A yellow precipitate formed after approximately two hrs. The mixture was allowed to cool to room temperature and filtered. The residue was washed with hot water, dried under reduced pressure at 100°C to give 60 percent of the theoretical amount of p-phenylenebisthiourea (7). The original filtrate was then heated at the reflux temperature for an additional 12 hrs, then cooled, filtered and the residue dried as before. An additional 25 percent of 7 was thus obtained.

A solution of 2.3 mole of bromine in chloroform was slowly added to a slurry of one mole of the bisthiourea 7 in chloroform. The resulting mixture was stirred for 16 hrs at room temperature, then heated gently to the reflux temperature. Gentle reflux was maintained for 24 hrs. Vigorous reflux was then maintained for 7 hrs. The resulting perbromide of 8 was collected by filtration and washed with chloroform. The free amine 8 was obtained by stirring the product with 2N ammonium hydrofide, filtering, and washing the gray residue with water. Three recrystallizations from glacial acetic acid and activated charcoal afforded a 45-50 percent yield of 8 as colorless needles after drying at 100°C under reduced pressure.

The diaminobenzobisthiazole 8 was hydrolyzed to the potassium salt of monomer 6 by the following method. A mixture of compound 8 and 21N potassium hydroxide was heated at the reflux temperature for 5 hrs. The resulting yellow solution was allowed to stand and cool overnight. The large prisms that formed were collected under an inert atmosphere by filtration. Conversion to the dihydrochloride salt 6 was performed by transferring the crystals into a flask containing a solution of dilute hydrochloric acid and 5 percent stannous chloride. The resulting bright yellow slurry was heated to a pot temperature of 70°C and an equal volume of concentrated hydrochloric acid was then added. The resulting pale yellow crystals were collected by filtration, pressed as dry as possible and washed with diethyl ether. The monomer was then recrystallized twice again by stirring with dilute hydrochloric acid containing 5 percent stannous chloride, heating to 70°C, and adding an equal volume of concentrated hydrochloric acid. The colorless crystals were then collected

by filtration, pressed as dry as possible, washed with diethyl ether, and then dried to constant weight at 25°C under reduced pressure (<0.05 torr).

B. PBT Synthesis

Successful high molecular weight PBT preparation is dependent on careful execution of each of the following steps:

- Both monomers must be carefully dried. Monomer 6 was dried at room temperature under reduced pressure to prevent loss of hydrogen chloride which takes place at elevated temperatures. Terephthalic acid was dried at 110°C under reduced pressure.
- The terephthalic acid must be of fine particle size. The initial reaction of monomers is heterogeneous in nature and thus is dependent on particle size. If the particle size is too large, the temporary stoichiometric imbalance may result in decomposition of the other monomer if the temperature of the reaction rises above 150°C before the imbalance is rectified.
- Exact stoichiometry of monomers is essential.
- Sufficient reaction time at 180°C is necessary, regardless of the bulk viscosity of the polymerization mixture. It appears that the molecular weight continues to increase in samples that are too viscous to be stirred when they are heated without stirring at 180°C.

The PBT polymerizations conducted under this contract are listed in Table 1.

The following experimental procedure used commercially available terephthalic acid, 99+ percent, that had been dried overnight under reduced pressure at 100°C, and diaminobenzenedithiol monomer that had been recrystallized twice. The second recrystallization from hydrochloric acid and stannous chloride was carried out without the use of an inert atmosphere glove bag. The polyphosphoric acid (PPA) was prepared from 85 percent phosphoric acid and phosphorus pentoxide just prior to use.

To a 500 ml resin kettle that had been flamed and purged with argon was added 4.21306 g (0.017183 mol) of 2,5-diamino-1,4-benzenedithiol dihydrochloride. PPA (245 g) was added and the resultant white, bubbly slurry was stirred under a slow stream of argon according to the following schedule:

Temp, °C	Duration, hrs	Remarks
RT	21.5	Solution became clear
50	5	Bubbling resumed
70	20	Solution became clear

Table 1

PBT POLYMERIZATIONS

PBT No.	Polymer Conc, Percent	Yield, G	Dehydrochlorination Time, Hrs RT-50°C	Dehydrochlorination Time, Hrs 50-90°C	Polymerization Time, Hrs	Intrinsic Viscosity DL/G (MSA, 30°C)
20	3.1	2.4	24	12	8	6.2
23	1.5	6.9	24	7	20	11.2
31	1.0	7.4	--	20	29	2.0
32	1.5	7.5	18	24	24	2.1
38	1.5	4.8	--	45	26	4.7
43	1.4	5.9	48	6	22 + 3	9.0
47	1.2	4.6	26	18	31 + 17	10.7
53	1.2	71.0	53	6	25 + 18	14.0
55	3.0	8.2	24	24	19 + 18	15.6
57	2.2	124.2	54	2	23 + 15	18.0
62	5.05	20.3	24	5	12 + 29*	26.5

Terephthalic acid (2.85458 g, 0.017183 mol) was then added as a powder and the mixture was stirred to give a homogeneous slurry. Additional PPA (82.5 g) was then added and heating under argon was continued according to the following schedule:

Temp, °C	Duration, hrs	Remarks
70	1	
85	1	HCl still detected in argon stream
100	3.5	
130	2	27.5 g PPA added, HCl still detectable
150	7.5	
165	7	48 g PPA added (Polymer conc = 1.16 percent)
180	4.5	
190	5	Balling up on stirrer

At this point, the polymerization medium was dark amber with deep blue green fluorescence. The temperature was reduced to 180°C and the stirrer was stopped. The mixture was stirred three times for several minutes at a time during the next 17 hrs. Methanesulfonic acid (MSA, 135 g) was then added and stirred. The lumpy mixture was poured into 3 liters of methanol, filtered, and then washed with methanol. After brief drying in an oven the polymer was dissolved in 2000 g of MSA and precipitated into 9 liters of water containing 1 liter of ammonium hydroxide.

The golden yellow polymer was collected by filtration, was washed successively with water, methanol, methanol-benzene mixtures, and finally benzene and then was freeze-dried from benzene. Final drying was carried out at 80°C/0.1 mm for 12 hrs. The polymer was coded PBT-2122-47.

The following viscosity data was measured in MSA and 30.0°C:

c, g/dl	$\eta_{sp}/c = \eta_{red}$	$\ln(\eta_{rel})/c = \eta_{inh}$	$[\eta]$
0.15605	20.06	9.09	
0.10403	16.60	9.64	10.7
0.07802	15.21	10.03	

The polymerization conducted in PPA at a polymer concentration of 3 percent (PBT-2122-55) proceeded much faster than polymerizations at concentrations of 1.5 percent. The polymerization medium was very mobile at temperatures between 90° and 160°. The medium became homogeneous after reaction at 150°, and its bulk viscosity then increased rapidly. After it was stirred at 190° for a short time, the polymerization medium was dark amber, clear, and gel-like in appearance.

Attempts to obtain fine line spectra of the PBT polymer by ^{13}C or ^{1}H nmr failed. The solvent was prepared by adding 15 percent D_2O to chlorosulfonic acid. A broad resonance from 130 to 160 ppm downfield from TMS was obtained by ^{13}C nmr at 30°C. The spectra was rerun at 60°C in an attempt to increase polymer mobility. No appreciable change was seen in the spectrum. Bulk viscosity was high for the 3 percent solution used, but the TMS signal was sharp. Thus, restricted tumbling motion of the PBT polymer was one explanation for the broad line width. The proton nmr spectrum showed no proton peaks due to polymer. More concentrated solutions with higher D_2O content may be necessary. The ^{13}C nmr spectrum of the model compound was obtained in $ClSO_3H/D_2O$. The spectrum and assignments are shown in Figure 3. The broad line spectrum of the polymer is shown to envelop the fine line spectrum of the model compound (see Figure 4).

Elemental Analysis of PBT-2122-23 gave the following results:

Anal. Calcd for $C_{14}H_6N_2S_2$: C, 63.13; H, 2.27; N, 10.51; S, 24.08
C, 61.75; H, 2.46; N, 10.24; S. 23.22

C. The Ames Salmonella/Microsome Test

We conducted the Ames test for mutagenic activity using five strains of Salmonella typhimurium on three compounds:

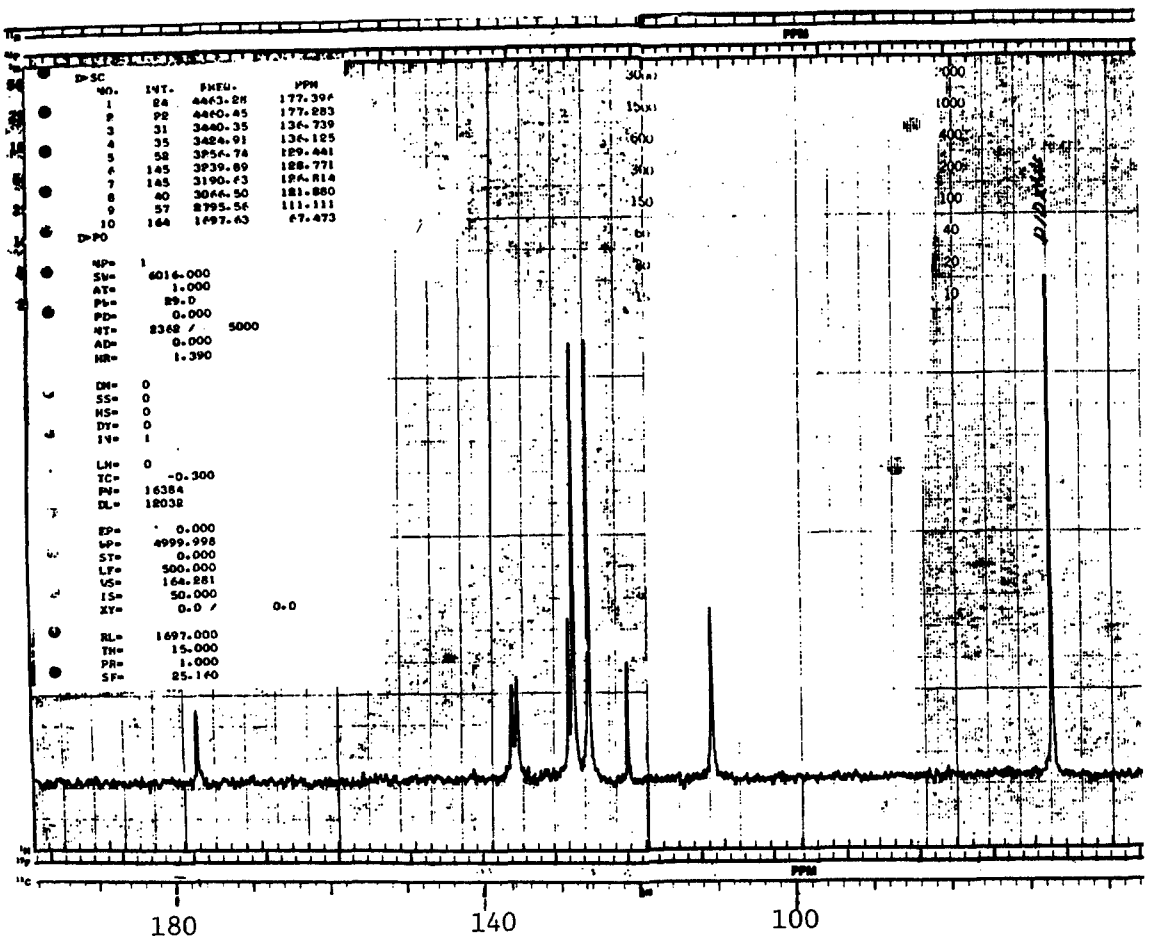
4,6-Diaminoresorcinol dihydrochloride

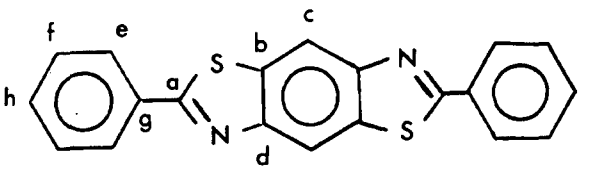
2,6-Diaminobenzo[1,2-d:4,5-d']bisthiazole, (8)

2,5-Diamino-1,4-benzenedithiol dihydrochloride, (6)

There is a high correlation between mutagenicity in the test bacteria and carcinogenicity in humans. Approximately 85 percent of the compounds that prove to be mutagenic by the Ames test are also carcinogenic. However, not all carcinogens are mutagenic, though there is a high correlation in this direction also.

The results of three sets of experiments with the five strains of bacteria are shown in Tables 2 to 7. The negative controls on these tables give the background levels of mutations for the five strains





*	ppm, downfield from TMs	Assignment
s	177.4, 177.3	a
s	136.7	b
d	136.1	c
s	129.4	d
d	128.8	e
d	126.8	f
s	121.9	g
d	111.1	h

*Resonance Decoupling, s = singlet or quaternary carbon, d = doublet or tertiary carbon

Figure 3 ^{13}C-nmr of 2,6-Diphenylbenzo[1,2-d:4,5-d']bisthiazole and Assignments

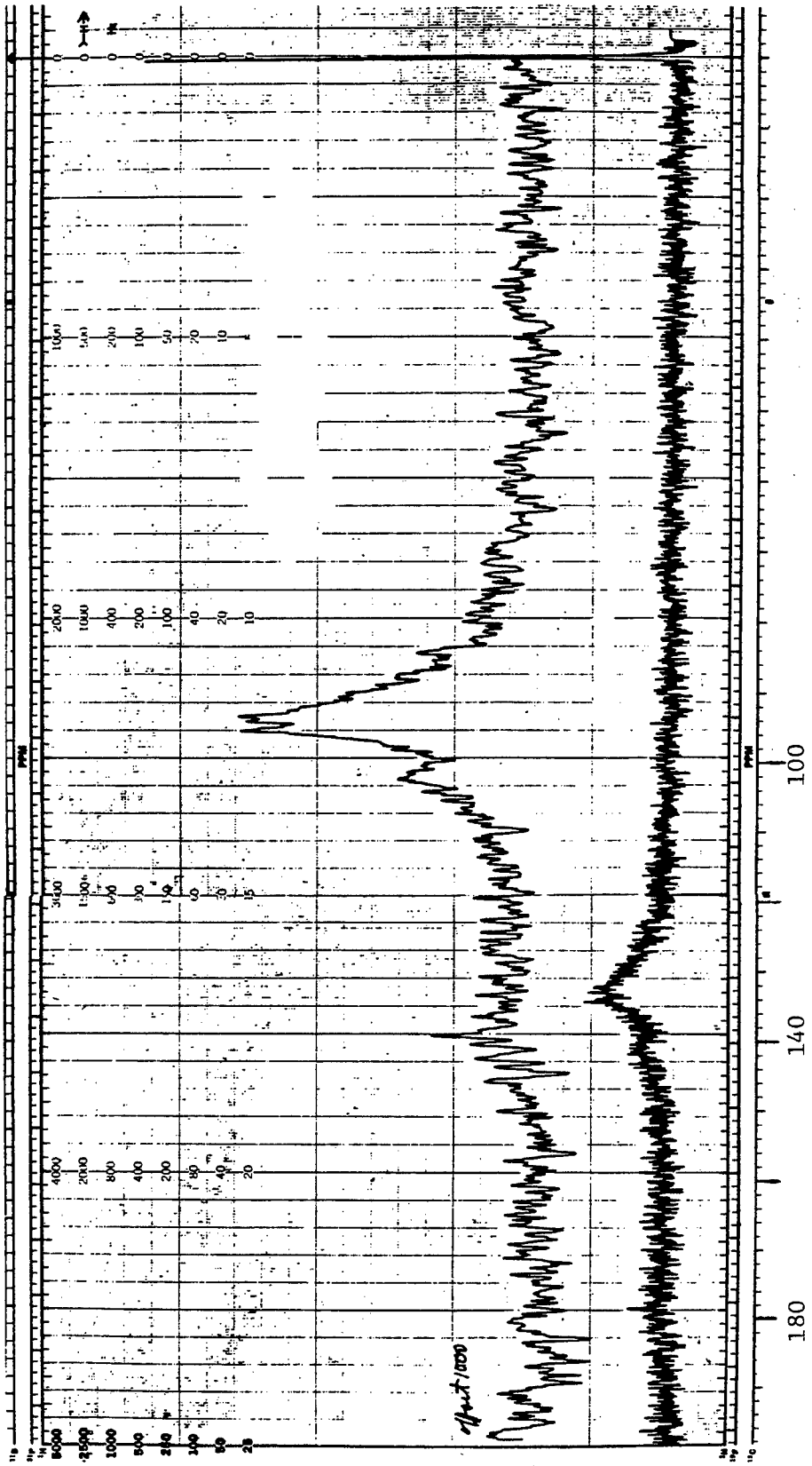


Figure 4. ^{13}C-nmr of PBT in Chlorosulfonic Acid/D_2O
Reference = TMS

Table 2

IN VITRO ASSAYS WITH SALMONELLA TYPHIMURIUM
2,6-DIAMINOBENZO[1,2-d:4,5-d']BISTHIAZOLE, 4,6-DIAMINORESORCINOL DIHYDROCHLORIDE,
AND 2,5-DIAMINO-1,4-BENZENEDITHIOL DIHYDROCHLORIDE
Experiment 1

Compound	Metabolic Activation	Micrograms of Compound Added per Plate	Average Histidine Revertants per Plate TA1535	TA1537	TA1538	TA98	TA100
Negative controls							
DMSO	-	50,000	31	25	17	15	100
	+	50,000	14	17	20	27	87
H_2O	-	50,000	23	24	13	22	118
	+	50,000	14	17	24	34	98
Positive controls							
Sodium azide	-	1	459				484
9-Aminoacridine	-	50		136			
2-Nitrofluorene	-	5				956	
2-Aminoanthracene	+	2.5	197	180	690	912	676
2,6-Diaminobenzo[1,2-d:4,5-d']	-	1	31	13	9	19	98
bisthiazole	-	25	28	11	12	15	117
Solvent: DMSO	-	100	26	16	11	18	121
	-	500	28	18	9	25	115
	-	1000	26	14	14	25	108
	-	2500	28	12	10	15	112
	-	5000	28	14	11	26	112
	+	1	11	18	39	31	92
	+	25	11	15	39	31	113
	+	100	8	23	20	29	112
	+	500	8	15	28	31	107
	+	1000	14	14	23	31	94
	+	2500	12	20	21	30	107
	+	5000	16	23	22	36	111

Table 2 (concluded)

Compound	Metabolic Activation	Micrograms of Compound Added per Plate	Average Histidine Revertants per Plate TA1535	TA1537	TA1538	TA98	TA100
4,6-Diaminoresorcinol dihydrochloride Solvent: H_2O	-	1	26	15	10	18	114
	-	25	29	17	17	30	126
	-	100	23	23	8	32	120
	-	500	16	21	10	33	143
	-	1000	18	14	T*	22	181
	-	2500	12	4T	T	T	146
	-	5000	3T	T	T	T	141
	+	1	11	25	113	43	130
	+	25	11	22	125	41	131
	+	100	12	21	43	36	137
	+	500	13	23	40	41	142
	+	1000	18	45	27	70	191
	+	2500	10	11	19	35	245
	+	5000	10	3T	T	13T	217
2,5-Diamino-1,4-benzenedithiol dihydrochloride Solvent: H_2O	-	1	28	15	14	20	110
	-	25	23	14	12	20	136
	-	100	24	17	11	29	125
	-	500	30	15	13	23	138
	-	1000	28	17	10	26	105
	-	2500	22T	6T	3T	16T	84T
	-	5000	11T	T	T	3T	63T
	+	1	7	18	11	33	99
	+	25	10	25	21	32	111
	+	100	11	29	18	34	136
	+	500	9	30	21	40	122
	+	1000	10	18	19	41	100
	+	2500	16	18	15T	32	82
	+	5000	8T	14T	13T	30	73T

* T, toxic.

Table 3

IN VITRO ASSAYS WITH SALMONELLA TYPHIMURIUM

2,6-DIAMINOBENZO[1,2-d:4,5-d']BISTHIAZOLE AND 4,6-DIAMINORESORCINOL DIHYDROCHLORIDE

Experiment 2

Compound	Metabolic Activation	Micrograms of Compound Added per Plate	Average Histidine Revertants per Plate TA1535	TA1537	TA1538	TA98	TA100
Negative control	-	50,000	25	6	12	13	114
DMSO	+	50,000	16	14	26	29	82
Positive controls							
Sodium azide	-	1	439				478
9-Aminoacridine	-	50		96			
2-Nitrofluorene	-	5			772	339	
2-Aminoanthracene	+	2.5	130	73	461	1150	771
2,6-Diaminobenzo[1,2-d:4,5-d']	-	1	24	6	12	30	107
bisthiazole	-	25	28	9	13	28	125
Solvent: DMSO	-	500	30	8	12	29	102
	-	1000	25	5	8	25	104
	-	2500	22	4	7	17	93
	-	5000	19	7	6	19	134
	+	1	14	14	23	42	83
	+	25	8	13	20	38	84
	+	500	11	10	22	37	106
	+	1000	12	13	19	42	92
	+	2500	11	13	16	48	105
	+	5000	8	14	18	31	83

Table 3 (concluded)

Compound	Metabolic Activation	Micrograms of Compound Added per Plate	Average Histidine Revertants per Plate				
			TA1535	TA1537	TA1538	TA98	TA100
4,6-Diaminoresorcinol dihydrochloride	-	1	31	7	11	19	123
	-	25	26	4	13	26	104
Solvent: DMSO	-	500	23	7	T*	27	113
	-	1000	T	5T	T	5T	139
	-	2500	T	T	T	T	135T
	-	5000	T	T	T	T	T
	+	1	14	16	18	30	100
	+	25	13	21	32	42	82
	+	500	14	21	22	59	98
	+	1000	11	28	20	60	143
	+	2500	3T	20T	14T	51	138
	+	5000	6T	9T	13T	29T	125

* T, toxic.

Table 4

IN VITRO ASSAYS WITH SALMONELLA TYPHIMURIUM
2,5-DIAMINO-1,4-BENZENEDITHIOL DIHYDROCHLORIDE

Experiment 2

Compound	Metabolic Activation	Micrograms of Compound Added per Plate	Average Histidine Revertants per Plate TA1535	TA1537	TA1538	TA98*	TA100
Negative control	-	50,000	18	5	9		100
Warm distilled H_2O	+	50,000	16	7	16		95
Positive controls							
Sodium azide	-	1	292				548
9-Aminoacridine	-	50		212			
2-Nitrofluorene	-	5			1731	911	
2-Aminoanthracene	+	2.5	269	98	1154	1673	1465
2,5-Diamino-1,4-benzenedithiol dihydrochloride	-	1	18	8	9		108
	-	25	25	7	12		126
Solvent: Warm distilled H_2O	-	500	16	8	7		118
	-	1000	20	6	5T†		78T
	-	2500	5T	4T	T		T
	-	5000	T	T	T		T
	+	1	21	10	19		124
	+	25	10	11	23		147
	+	500	11	13	26		129
	+	1000	13	10	16		99
	+	2500	5T	9	15T		1T
	+	5000	T	6T	7T		T

* Strain contaminated.
† T, toxic.

Table 5

IN VITRO ASSAYS WITH SALMONELLA TYPHIMURIUM
2,5-DIAMINO-1,4-BENZENEDITHIOL DIHYDROCHLORIDE

Experiment 3

Compound	Metabolic Activation	Micrograms of Compound Added per Plate	Average Histidine Revertants per Plate TA98
Negative control	-		22
Warm distilled H_2O	+		34
Positive controls			
2-Nitrofluorene	-	5.0	345
2-Aminoanthracene	+	2.5	852
2,5-Diamino-1,4-benzenedithiol dihydrochloride	-	1	21
	-	25	23
Solvent: Warm distilled H_2O	-	500	31
	-	1000	34
	-	2500	14T*
	-	5000	3T
	+	1	28
	+	25	28
	+	500	37
	+	1000	34
	+	2500	39
	+	5000	43

* T, toxic to bacteria indicated by pinpoint colonies and/or clearing of background lawn.

Table 6

IN VITRO ASSAYS WITH SALMONELLA TYPHIMURIUM STRAIN TA100
4,6-DIAMINORESORCINOL DIHYDROCHLORIDE

Experiment 3

Compound	Metabolic Activation	Micrograms of Compound Added per Plate	Average Histidine Revertants per Plate	
			Solvent DMSO	Solvent H_2O
Negative control (solvent alone)	-		119	146
	+		105	110
Positive controls				
Sodium azide	-	1.0	637	
2-Aminoanthracene	+	2.5	895	
4,6-Diaminoresorcinol dihydrochloride	+	1	105	120
	+	25	104	127
	+	500	153	158
	+	1000	148	172
	+	1500	178	271
	+	2000	188	290
	+	2500	166T	234
	+	5000	138T	251

* T, toxic to bacteria indicated by pinpoint colonies and/or clearing of background lawn.

TABLE 7

IN VITRO ASSAYS WITH SALMONELLA TYPHIMURIUM STRAIN TA98
4,6-DIAMINORESORCINOL DIHYROCHLORIDE

Experiments 3 and 4

Compound	Metabolic Activation	Micrograms of Compound Added per Plate	Average Histidine Revertants per Plate	
			Solvent DMSO	Solvent H_2O
Experiment 3				
Negative control (solvent alone)	-		17	17
	+		30	25
Positive controls				
2-Nitrofluorene	-	5.0	577	
2-Aminoanthracene	+	2.5	1091	
4,6-Diaminoresorcinol dihydrochloride	+	1	26	23
	+	25	19	33
	+	500	51	44
	+	1000	59	46
	+	2500	22T*	18T
	+	5000	13T	T
Experiment 4				
Negative control (solvent alone)	-		19	22
	+		23	34
Positive controls				
2-Nitrofluorene	-	5.0	345	
2-Aminoanthacene	+	2.5	852	
4,6-Diaminoresorcinol dihydrochloride	+	1	30	30
	+	25	40	38
	+	500	81	76
	+	1000	29T	72
	+	1500	10T	17T
	+	2000	T	18T
	+	2500	T	9T
	+	5000	T	4T

* T, toxic to bacteria indicated by pinpoint colonies and/or clearing of background lawn.

under test conditions. The positive controls show the level of mutagenicity of four known mutagens to the various strains. Table 2 lists results from the first set of experiments for the three compounds. No dose-related increase in the number of mutants (histidine revertants) was seen with 2,6-diaminobenzo[1,2-d:4,5-d']bisthiazole in any of the five strains; this compound was not toxic to the bacteria up to 5 mg/plate. The PBT monomer, 2,5-diamino-1,4-benzenedithiol dihydrochloride, did not cause any dose-related mutagenicity, and was toxic to the bacteria at about 2.5 mg/plate. The PBO monomer, 4,6-diaminoresorcinol dihydrochloride, caused a slight, dose-related increase in revertants in one of the five strains (TA100), and was toxic to the bacteria at about 2.5 mg/plate.

Tables 3 and 4 show the results of the second set of experiments for the three compounds. Again, no dose-response nor toxicity was seen in any strain with the benzobisthiazole (Table 3). The slight mutagenic dose-response seen in strain TA100 with 4,6-diaminoresorcinol dihydrochloride in the first test was not observed in the second test. However, a slight mutagenic dose-response was observed in strain TA98 (Table 3). The solvent used in the first test was water, and DMSO was the solvent used in the second test. Further testing is now in progress to further investigate the effects of 4,6-diaminoresorcinol dihydrochloride with TA98 and TA100 in both solvents.

Table 4 presents the results of the second test with 2,5-diamino-1,4-benzenedithiol dihydrochloride. As in the first test, the compound caused no mutagenic dose-response and was toxic at about 2.5 mg/plate.

Table 5 presents the results of the final experiment with 2,5-diamino-1,4-benzenedithiol dihydrochloride in which Salmonella typhimurium strain TA98 was used with and without metabolic activation. This compound was not mutagenic. It was toxic at about 2.5 mg/plate without metabolic activation, but it did not appear to be toxic at any dose tested with metabolic activation. These results confirm results from our previous experiments with this compound.

Tables 6 and 7 present the results of the final experiments with 4,6-diaminoresorcinol dihydrochloride, which was dissolved in two different solvents, with metabolic activation. Dose-related increases in revertants were observed in strain TA100 when the compound was dissolved in either H_2O or DMSO (Table 6). However, the increases were greater when H_2O was used as solvent. Dose-related increases in revertants were also observed in strain TA98 (Table 7) when the compound was dissolved in either H_2O or DMSO. The increases were about the same in this strain with both solvents.

D. Attempted Polymerization of 2,5-Diaminohydroquinone with Terephthalic Acid

2,5-Diaminohydroquinone (obtained from AFML) was recrystallized twice from aqueous stannous chloride/hydrochloric acid. Elemental analysis of the monomer agreed very well with the formula for the dihydrochloride salt. The slightly off-white monomer was placed in freshly prepared 85 percent PPA and warmed to 60°C to initiate dehydrochlorination. The mixture became purple after 2 hrs, indicating the formation of side-products. After the foaming subsided, a stoichiometric amount of terephthalic acid was added, and the mixture was slowly heated to 130° and then heated at 150° overnight. The terephthalic acid dissolved completely but the mixture did not become viscous. After normal work up, the product was black and nonpolymeric in appearance. It was concluded that the hydroquinone monomer was not stable in the PPA under reaction conditions, leading to a severe imbalance in the stoichiometry.

IV CONCLUSIONS AND RECOMMENDATIONS

High molecular weight PBT can be prepared by a batch process in polyphosphoric acid at polymer concentrations greater than 3 percent. We believe that PBT is an excellent candidate for future development as a structural material with superior mechanical properties.

The measured intrinsic viscosity of PBT is highly dependent on the solution history of the sample. Standardization of work-up procedures, especially concentrations and water content of MSA reprecipitations, will be necessary in future work, if intrinsic viscosity is to be used as an accurate measure of a sample's molecular weight distribution.

The PBT monomer, 1,4-diamino-2,5-benzenedithiol dihydrochloride, and its precursor, 2,6-diamino-benzobisthiazole, are non-mutagenic as determined by the standard Ames Salmonella/microsome test. According to our tests, which should be considered preliminary, these compounds should pose no carcinogenic hazard to workers. The PBO monomer, however, shows slight mutagenic activity under the same tests. Work with this compound should proceed with the necessary precautions to eliminate exposure to workers.

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PHASE II: FABRICATION AND EVALUATION

I INTRODUCTION

The Air Force Materials Laboratory (AFML) has developed numerous polymer systems with unique potential for structural adhesive and advanced composite applications. Among these systems are thermally stable polymers, moisture-resistant systems, cryogenic resins, long-flow-time materials, and limited-flow polymers. Unfortunately, these systems have sometimes failed to reach the appropriate development areas where their potential could be fully evaluated. The difficulty lies in evaluating the new resins for composite and adhesive applications when only small samples of uncharacterized polymer systems are available. Systems that are otherwise of value are often discarded because of problems that have little to do with the polymer itself. Most composite and adhesive systems now in use exhibited low mechanical properties and disappointing performance when first evaluated.

The objective of this work is to identify, analyze, and solve the material problems associated with new polymer systems. We strive to avoid pursuing polymers with little potential value, and to avoid discarding systems that promise to fill Air Force needs.

II SUMMARY

A. Polyimide Films

Polyimide resins are of great interest to the aerospace industry. Their excellent thermal/oxidative resistance and mechanical properties make them attractive candidates as composite matrix resins and as structural adhesives.

In order to determine and compare properties of several new polyimides, thin films are needed to prepare test specimens. Films were prepared from several polyimide resin samples. Special techniques were developed to handle polyimides with out-gassing problems, low surface tension properties, several amorphous/crystalline solid state forms, and extremely narrow processing windows.

B. RPS Resin/P-1700 Composite Matrix Resins

Thermoplastic matrix resins have significant potential for reducing the cost of composite structures. Recent studies[1-6] have demonstrated cost saving in the range of 25 to 80 percent over conventional composites, and often 20 to 40 percent over aluminum aircraft structure. These savings are a result of novel manufacturing techniques, such as quick consolidation, vacuum forming, postforming, hot stamping, and ultrasonic welding. These processes require seconds rather than the hours required by conventional techniques. Furthermore, thermoplastic matrix resins are tough, and distribute stress well. They offer significant advantages in environmental resistance, and eliminate the need for costly autoclave facilities and slow, expensive hand layup/vacuum bag manufacturing approaches. However, these materials are not without drawbacks. Processing temperatures are usually 150 to 250 degrees Farenheit above the glass transition temperature (T_g). Thus, a 350°F service resin system requires a 600°F processing temperature. Additionally, high temperature performance drops significantly at temperatures approaching T_g, limiting the usefulness of the material.

Plasticizers may be used to reduce the processing temperatures of thermoplastics, but they also reduce the end-use temperature. A concept suggested by AFML is to use a reactive plasticizer that lowers the T_g of the thermoplastic during processing; then becomes dormant by reacting either with itself or with the host thermoplastic. In the former case, it becomes an inert filler; in the latter, it may raise the T_g of the final material, improving both the processing characteristics and the end-use potential of the host thermoplastic. Work described in this report deals with the continuation and conclusion of our study in the

use of TPS with a polysulfone matrix to test the feasibility of the reactive plasticizer concept. Levels of RPS were increased until we measured, in effect, the use of polysulfone diluent as a toughening agent for a pure RPS matrix. The performance of the various resin blends was compared with that of pure RPS and pure P-1700 polysulfone resins.

C. Laminating Resins Containing Aromatic Enyne Linkages

In recent years, AFML has developed a new approach for curing heterocyclic polymers based on intramolecular cycloaddition reactions (IMC). In this approach, a cyclic aromatic system is formed within the polymer backbone, stiffening the polymer chain and significantly raising the glass transition temperature, T_g.

One attractive linkage for investigation is the enyne linkage (Figure 1). This was successfully incorporated into a polysulfone polymer backbone at AFML. Polysulfone polymers containing various levels of enyne linkages were evaluated by SRI and their performance was compared to that of unmodified polysulfone polymer.

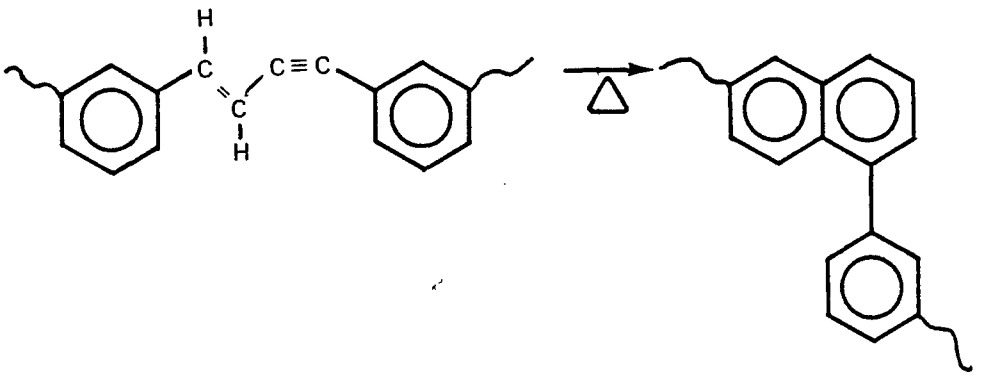


Figure 1 Enyne Linkage and Cure

III TECHNICAL DISCUSSION

A. PI Films

1. Thermid 1739 Films

At the end of the last reporting period,[9] we successfully fabricated a 5-mil film of Thermid 1739, an improved, solvent free acetylene terminated polyimide. The following procedure was used.

To avoid oxidative degradation, we used a vacuum bag technique. The Thermid powder was placed between Frekote-surfaced Kapton film, next between caul plates, and the assembly was placed into a press at 350°F, then heated to 600°F. After a 2-hour hold at 600°F, the film was slowly cooled under pressure and vacuum. A clear, amber 5-mil film was produced that appeared to be of high quality. It was returned to AFML for evaluation.

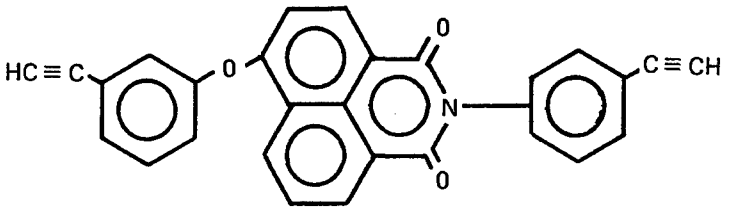
Two more films were made from the sample of Thermid 1739 and sent to AFML. They were fabricated using previously reported processing conditions. Special efforts were taken to prevent air entrapment. The films appeared to be of high quality.

2. Evaluation of Polyimides with Six Member Rings

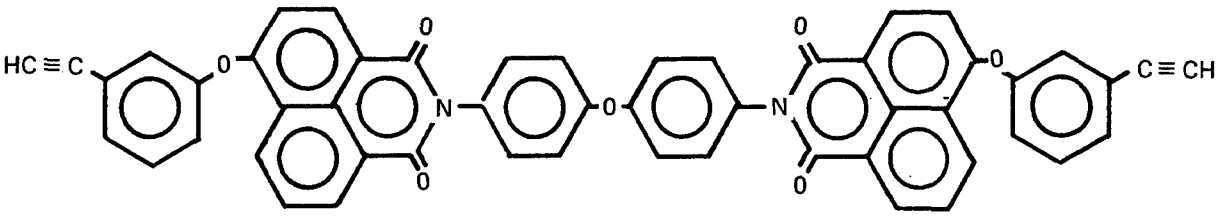
Samples of two compounds (designated No. 1813 and No. 1805) were received from AFML. Figure 2 gives their structures. These oligomers contain six-membered imide rings that may show improved hydrolytic stability when compared with conventional polyimides. Our first objective was to prepare neat resin films so that dynamic mechanical properties can be determined and compared to those of conventional polyimides. We began our evaluation of PI No. 1813 by attempting to fabricate high quality films.

The DSC data on No. 1813 show melting at 202°C and the onset of polymerization at about 208°C (DSC heating rate = 20°C/min). The proximity of the two temperatures prompted a preliminary investigation of flow properties to determine if a film could successfully be formed before excessive cure occurred.

A Fisher-Johns melting point apparatus was used to qualitatively determine the viscosity of the resin melt. A few crystals of No. 1813 were placed on the block and heated at approximately 1-2°C/min through 210°C. The sample melted without flow between 195°C and 206°C. At 202°C, the crystals turned brown and became powdery upon further heating.



Compound No. 1813



Compound No. 1805

Figure 2 Structures of 1813 and 1805

It seems that cure begins to occur before melting occurs and necessitates a rapid heatup rate.

Subsequently, crystals were dropped on a 232°C melting point block. The sample melted and flowed immediately. This experiment was repeated at 206°C with the same results.

A trial film was made using techniques similar to those for Thermid 1739 (see Table 1). The resulting film was dark and brittle, and contained numerous voids. We found four pieces of a glass-like substance that prevented the coals from closing to the stops. We then sieved the remaining resin through a 40-mesh screen and found more glass-like pieces. We next sieved all the resin through a 325-mesh screen that removed additional fine particles.

A second film was made using the same conditions as the first film except that the pressure was increased to 6.89 MPa (1000 psi). This film was inspected after 4 hrs at 232°C and was found to be a little lighter in color and not quite as brittle as the previous films. It had two large voids, several small voids, and some pinholes. (The pinholes may be due to very small bits of the glass-like material.) Resin

Table 1

CONDITIONS OF TRIAL NO. 1813 FILM

Layup	Cure Schedule
Kapton bag	Apply vacuum
Two plies glass cloth	Have press at 232°C
Caul	Place assembly in hot press
1 ply Frekoted Kapton 0.013 cm (5 mil) spacers* and resin	After temperature equilibrates, apply 2.76 MPa pressure (400 psi)
1 ply Frekoted Kapton base caul and sealant	Hold 4 hours Heat to 371°C Hold overnight (~16 hrs) Cool slowly with vacuum and pressure

*Spacers were 13 cm long and 5 cm apart.

flowed under and over the 0.013-cm (0.005 in.) spacer, causing uneven film thickness.

The film was rebagged and the cure cycle was completed. As expected, the film darkened a little and became more brittle. We decided to remove all glass-like material from the resin and devise an alternative spacer system.

The resin was dissolved in THF, filtered, and precipitated in water. We then dried the resin for approximately 36 hrs at 23°C under vacuum.

We investigated a new spacer system, consisting of polyethylene spacers. The results were the same; there was flow both under and over the spacers, resulting in an uneven film.

We next tried a spacer system consisting of 0.015-cm (0.006-in.) polyethylene shims placed only under the corners of the caul with no restraint to flow. An even film was obtained with this technique, but problems in porosity persisted.

We again checked the flow time of the system at two temperatures--200°C and 232°C. Crystals of resin were dropped onto a cover glass on the hot melting point block, and immediately (~3 sec) the cover glass was dropped into THF. The amount of cure is measured by the amount of undissolved residue on the cover glass. At 200°C most of the sample dissolved, and at 232°C there was no apparent dissolution. This indicates that at 232°C, the flow time of the system is very short (seconds)

at best; thus, to obtain the maximum amount of flow life, an initial cure temperature as near as possible to melt point is desirable.

We made a third film, using 0.015-cm (0.006-in.) spacers in the corners, using the filtered oligomer. The layup and cure cycle were the same as the first film except that this film was inspected after 4 hrs at 232°C. Flow was excessive, producing an unsatisfactory film that was also excessively porous.

To eliminate the possibility of solvent causing the voids, we heated the resin overnight at 74°C (5° higher than the boiling point of THF) under vacuum.

We next investigated a variety of processing conditions, using small amounts of resin. We found that molten resin had a high surface tension and very low viscosity. It formed high beads readily on Teflon and Frekote surfaces. Films could not be cast from the resins; pressure was needed to flatten the resin into a film.

We made several attempts to press films from small amounts of resins, using a brief staging time at lower temperatures to reduce flow. These trials were unsuccessful and produced thick films with some small voids. The voids appear to be of two types:

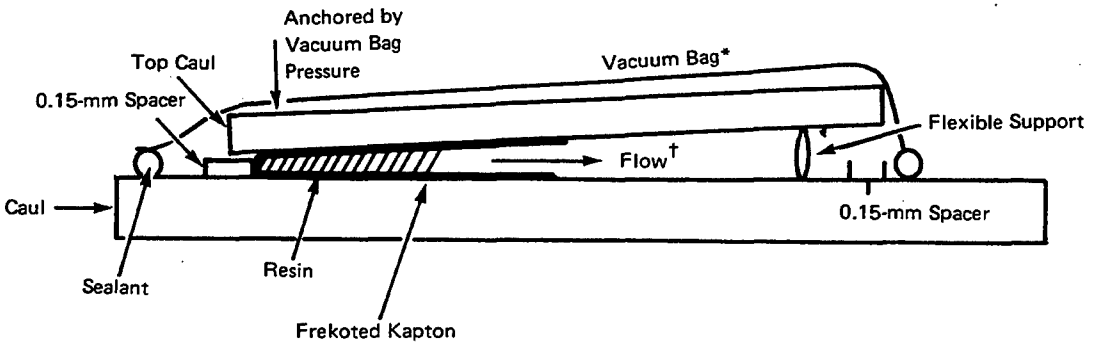
(1) Irregular voids that appear to result from high flow and low viscosity when the resin is molten

(2) Spherical voids, as might be attributed to residual solvents.

Drying for periods of up to five days at 76°C under vacuum did not eliminate the spherical voids. An ITGA was also run for 4 hours at 203°C and did not show measurable weight loss. Therefore, the voids well attributed to the low viscosity and high flow, with perhaps a trace amount of highly interacting residual solvent present.

Experiment 2349-57 was devised to control the flow and accommodate viscosity. Figure 3 diagrams the experimental setup. Flow was allowed in one direction only (all other directions were dammed). Bleeder plies were used above the top caul. The setup and cure schedule were as follows:

Setup	Cure
Vacuum bag	Assembly was placed in press at indicated platen temperature.
2 plies 181 glass	Platens were closed immediately to 6.89 MPa (1000 psi).
Top caul	Held at temperature one-half hour.
Frekoted Kapton resin and spacers	Cooled slowly.
Frekoted Kapton	
Base caul and sealant	



*Bleeder plies were used above the top caul.

†Flow was allowed in one direction only. All other directions were dammed.

Figure 3 Setup of Experiment 2349-57

The resulting film was an improvement over previous efforts, as some of the material appeared to be of adequate quality for AFML evaluation. We produced several additional small film pieces to closely define the processing window (see Table 2) and found it to be very small. These marginal results led us to consider an alternative processing approach. After discussing the problem with the AFML monitor, we reviewed AFML DSC data, which indicated that the No. 1813 could be converted from a crystalline to an amorphous form by heating the oligomer to 203°C and rapidly quenching it. The amorphous form has Tg of 76°C, which should provide a reasonably large processing window. We decided to pursue that approach. Therefore, we began a study of processing parameters, using a melting point block apparatus. The results of the study, shown in Table 3, brought several important points to our attention.

First, a rapid heat-up rate may be essential because the cross-linking reaction occurs below the melting point. Second, it was necessary to know exactly when the resin reached the melt temperature; a small variation could not be tolerated. Finally, it was necessary to quench the melt rapidly in order to minimize the extent of cure. As with the crystalline material, precise control is required to achieve the desired results.

Following these guidelines, we vacuum bagged a small amount of crystalline 1813, using the procedure described in the previous report. The lower platen of the press was heated to 238°C, and the upper platen was heated to 221°C. A thermocouple was placed next to the sample and was connected to a strip chart recorder.

The vacuum bag assembly was placed in the hot press, and 71 kN (8 tons) of pressure was applied. The temperature of the sample was monitored on the recorder. When the temperature reached 213°C (after ~9.6 min), the vacuum bag was moved to a water-cooled press. Quenching was immediate, as indicated by the temperature recorder.

Table 2

PROCESSING FOR RESIN NO. 1813 AT THREE TEMPERATURES

Specimen	Initial Temp. Of Upper Platen (°C)	Initial Temp. of Lower Platen (°C)	Lowest Temp. of Upper Platen Following Insertion of Vacuum Bag	Lowest Temp. of Lower Platen Following Insertion of Vacuum Bag	Results
2349-64-1	218	227	213	204	Excessive flow produced void-filled film
2349-64-2	196	204	193	188	Center of film was melted and fused but not uniform in color. It was ringed by unmelted but cured crystals.
2349-64-3	213	216	196	192	Flow was excessive but covered only half the area of 2349-64-1 (above).

Table 3

CORRELATION OF TMA, SOLUBILITY, AND EXTENT OF CURE OF 1813

Melting Point Block Temperature (°C)*	TMA (°C)	Resultant Color	Solubility in THF
198	185	Light yellow, opaque	Soluble
202	105	Yellow, opaque	Soluble
204	80	Gold, opaque	Soluble
206	80	Gold, opaque	Soluble
206/1 min	--	Reddish brown, clear	Insoluble

*Small crystals of resin were dropped onto the melting point block, which was preheated to the temperature indicated in this table. The resin was pressed between cover glasses until melting occurred (generally 1-2 sec). The sample was immediately quenched. (The last sample was allowed to remain on the melting point block for 1 min.)

The resulting resin was the clear reddish-brown color associated with the cured resin. A TMA indicated a transition at 115°C, but a sample of the resin exhibited no visible softening or flow when placed on a 115°C melting point block. The solubility of the resin in tetrahydrofuran was tested; an insoluble clear reddish-brown portion (cured material) and a soluble yellow powder (presumably uncured material) were found. The presence of the cured material indicates that either the heating rate was too slow or the temperature was too high.

A series of attempts was made to convert the remaining crystalline material to the amorphous form, using increasingly severe processing conditions. Tables 4 and 5 summarize the processing extremes used. No visual evidence of cured resin was found in any run, and the thermomechanical analysis showed only minor amounts of cured resin and no crystalline 1813.

We successfully converted all the crystalline 1813 to the amorphous state ($T_g \simeq 80°C$) and then tried to form a film from it. The conditions are given in Table 6. The resin was quenched, and examination showed softening and some flow. The pile of powder became cohesive, but granular looking, and its color was somewhat darker. A TMA of the resulting resin showed a transition at ≃175°C.

Table 4

MILDEST CONDITIONS USED FOR CONVERSION OF CRYSTALLINE 1813 TO AMORPHOUS 1813

Vacuum Bag Assembly:

- Vacuum bag (Kapton)
- 2 plies 181 glass
- Top caul plate
- 1 ply Frekoted Kapton
- Resin, .15 mm shims and thermocouple
- 1 ply Frekoted Kapton
- Base caul

Cure Schedule:

- Preheat press platens
  Upper - 260°C
  Lower - 288°C
- Insert vacuum bag
- Apply 71,000 newtons of pressure
- Thermocouple reached 200°C in 1.75 min
- Quench in a water-cooled press

Table 5

FINAL CONDITIONS USED FOR CONVERSION OF CRYSTALLINE 1813 TO AMORPHOUS 1813

- Preheat press platens to ~270°C
- Insert vacuum bag* in press
- Apply 4,450 newtons of pressure
- Thermocouple reached 220°C in less than 2 min
- Maintain at 220°C for about 20 sec
- Quench in a water-cooled press

*The vacuum bag is the same as that in Table 2 except that the 0.15-mm shims have been removed and the thermocouple has been moved into a hole drilled in the upper caul plate.

Table 6

INITIAL CONDITIONS FOR PRESSING A FILM FROM AMORPHOUS 1813

- Preheat press platens to 100°C
- Place vacuum bag assembly in press (see Table 2)*
- Apply 71,000 newtons of pressure
- Maintain at the stabilized temperature (~116°C) for 10 min
- Quench between cold platens

*Thermocouple in the top caul plate.

Finally, this resin (T_g ~175°C) was processed into a film using the conditions shown in Table 7. The film was a clear reddish-brown, but there were areas that did not receive adequate pressure because of the shims. Those portions that received pressure were smooth and attractive; the remainder was coarse and granular.

We demonstrated that the latitude for processing amorphous 1813 is considerably greater than that for crystalline 1813. However, we did

Table 7

CONDITIONS FOR FINAL PRESSING OF AMORPHOUS 1813

- Preheat press
  Bottom platen - 296°C
  Top platen - 282°C
- Insert vacuum bag (see Table 2)*
- Apply 71,000 newtons of pressure
- Temperature rose to 260°C in 5 min†
- Maintain at 260°C for 4 hrs
- Cool slowly under vacuum and pressure

*Thermocouple is in the top caul.

†Actual final temperature was 270°C.

not have sufficient material available to continue the study and to establish the optimum conditions for forming a film from the material.

An additional sample of 1813, now designated BR-1-76, was obtained from AFML late in this reporting period.

We simplified the procedure for producing amorphous BR-1-76. The resin was spread very thinly on a piece of Frekoted Kapton. The assembly was placed on a hot (260°C) press platen until the resin melted and was immediately removed from the press and cooled. Under these conditions, the resin formed clear gold droplets with a Tg of 75°C and very minor TMA peaks at 188°C and 238°C. Using this form of the resin, we were easily able to press a good quality but extremely fragile film at 93°C.

Using the procedures developed above, we formed droplets of amorphous resin and made two 5 x 5 x .15 mm cavities. The resin was pressed into the cavities at 93°C to form films.

We cured these films at two different temperatures. Both films were placed in a preheated vacuum oven and cured 30 minutes. One was placed in a 260°C vacuum oven and resulted in a smooth dark film with evidences of volatiles and/or puddling. The second was placed in a 210°C oven and resulted in a very rough and uneven film with evidences of volatiles. Since neither of these schedules produced a good quality cured film, we began a melting point block study of the amorphous material.

For the study, we preheated the melting point block to various temperatures and this dropped small amounts of amorphous BR-1-76 onto the block. The results of this study can be found in Table 8. Notice that at 182°C the results are ambiguous.

Table 8

OBSERVATIONS OF AMORPHOUS BR-1-76
ON A HOT MELTING POINT BLOCK

85°C	2 hours	No change
150°C	1 hour	Became opaque and yellow
175°C		Some melting at the edges
180°C		Some melting at the edges
180°C	10 min	Resin darkened
182°C		Turned opaque and then darkened
182°C		Melted into a clear low viscosity melt

The situation was clarified by placing a small amount of amorphous BR-1-76 on a room temperature melting point block and then raising the temperature. The results are listed below:

RT	the original clear gold of amorphous BR-1-76
85°C	a slight coalescence at the edges, but no melting
110°C	the resin suddenly turned grainy, light yellow, and completely opaque
190°C	the opaque resin melted and flowed to form a clear gold droplet
210°C	the color of the resin darkened slightly; there were no evidences of bubble

From this study, three forms of uncured resin were encountered: (1) the original form which is a light yellow powder with a melting point of 202°C, (2) a second form which is gold and has a Tg of 75°C, and (3) a third form which is a light yellow powder and has a melting point of 190°C.

Based on these results, we prepared some amorphous BR-1-76 and a 5 x 5 x .15 mm cavity. A film of the amorphous resin was formed by pressing it into the cavity at 93°C. The film-cavity assembly was inserted into a 227°C press, held 20 minutes and then cooled slowly. The sequence of events was essentially the same as those observed when the resin was heated on the melting point block. The only difference was that a few bubbles were observed when the resin melted. This phenomenon caused two small holes in the resulting film which was otherwise smooth and even.

This experiment was repeated except that the film was heated and cured under vacuum. The resulting film was very rough and uneven and had evidence of escaping volatiles.

In order to fabricate good quality film it will be necessary to develop processing which takes into account the release volatiles. This will be pursued in future work.

B. Evaluation of Polyimide Oligomer No. 1805

We received the DSC and TMA data on the PI oligomer No. 1805 from AFML. The DSC showed a slight endotherm at 224°C with three overlapping peaks of polymerization at 246°C, 253°C, and 265°C. The cured resin showed only decomposition. The TMA of the oligomer showed a transition at 240°C.

We ran a few crystals of oligomer on a Fisher-Johns melting point block and found a relatively high melt viscosity, with a rapid cure occurring at the softening temperature, which was observed to begin at

about 270°C. We made a series of three small films, as summarized in Table 9. Higher platen temperatures appeared to give higher quality films.

We ran additional melting point runs, using a thermocouple to closely monitor the temperature, and decided to cure the next film at 343°C under vacuum.

A 5 cm by 2.5 cm film was prepared (sample 2349-63) and cured as described in Table 10. The film appeared to have a good color and appropriate thickness (15 mm). However, it warped and broke into several irregular pieces. We believe significant stresses were locked in during cure and cool-down.

We tried annealing a piece of the film at 316°C and cooling between cauls, under contact pressure, at <0.5°C per minute. There was no additional flow (none was expected), and the piece was still warped. However, it appeared to be less brittle and tougher after the annealing cycle.

We repeated the cure, incorporating an annealing step and a slow cool-down. The film had good even color, and it did not curl, but it again broke into several pieces.

The film pieces, however, were of a reasonable size, several cm across, and were suitable for testing at AFML. Pieces of 1805 film were fabricated and sent to AFML for evaluation. This concluded our effort on polyimide 1805.

C. Evaluation of Polyimide 1885

Resin 1885 is an acetylene-terminated polyimide with a five-member imide ring shown in Figure 4. Our first objective was to prepare neat resin films, so that dynamic mechanical properties could be determined.

According to DSC data provided by AFML, the melting point of the material prior to heat treatment was 162°C. Polymerization onset occurred at 170°C and the polymerization peak at 231°C (at a heating rate of 20°C/min). Since the polymerization onset temperature was so close to the melt temperature, AFML investigated heat treating as a means of altering the thermomechanical properties.

The following work was carried out by AFML. Two samples of resin 1885 were heated to 175°C, then one was cooled rapidly and one slowly. The DSC of the rapidly cooled sample showed a T_g at 27°C, slight exotherm at 95°C and two melting points, one at 140°C, the other at 155°C. The DSC of the slowly cooled sample showed only a T_g at 28°C.

We received a sample of heat-treated 1885. A TMA of this resin indicated mobility between 50°C and 150°C and a T_g at 243°C.

Table 9

CONDITIONS AND RESULTS FOR 1805 FILMS

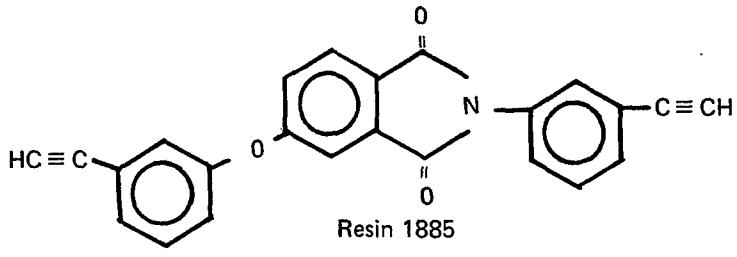
Specimen	Conditions	Results
2349-60-1	A small sample of resin and 0.15-mm shims were placed between pieces of Frekoted Kapton. This was placed between cauls, and the entire assembly was placed in a 300°C press. 7300 kg (8 tons) pressure was applied for 10 minutes. The assembly was removed and cooled in a water-cooled press.	The sample was 0.028-cm (0.011-in.) thick, mottled, and had either pinholes or specks of clear resin.
2349-60-2	Repeated 2349-60-1 (above) except the press was at 320°C and 10,900 kg (12 tons) of pressure was applied.	The sample was 0.019-cm (0.0075-in.) thick, mottled, and had spots of clear resin.
2349-61*	Repeated 2349-60-1 (above) except the press was at 330°C and the assembly was vacuum bagged and held 1 hour at room temperature. Upon insertion, the bottom platen dropped from 330°C to 282°C, and the top platen dropped to 310°C.	This film was more uniform in color, and was approximately 0.015-cm (0.006-in) thick. Around the edge of the film were unmelted, but cured, crystals. It looked as though molten resin broke through a dam of unmelted crystals, forming an appendage of greater uniformity.

*This assembly was placed in a press where it was possible to monitor the drop of platen temperature when the assembly was inserted. The other two assemblies were placed in another press.

Table 10

PREPARATION AND CURING OF SPECIMEN 2349-63

Vacuum Bag	Cure	Annealing
Kapton bag 2 plies 181 glass Top caul Frekoted Kapton Resin and shims Frekoted Kapton Base caul and sealant	Heat bottom platen to 371°C. Heat top platen to 356°C. Vacuum bag was placed in hot press and the press was closed at 6800 kg (7.5 tons). (Top platen dropped to 338°C and bottom platen dropped to 319°C.) Temperature of both platens was adjusted to 320°C. Held at 320°C one hour and then cooled.	Rebag film. Heat press with vacuum bag pressure to 343°C. Hold one-half hour. Cool slowly ≤0.5°C (1°F)/min.



Resin 1885

Figure 4 Resin 1885

A small sample of 1885 was vacuum-bagged as follows:

Kapton bag
2 plies 181 glass
Top caul with thermocouple
Frekoted Kapton resin and Armalon spacer
Frekoted Kapton
Base caul

The assembly was inserted in a 190°C press and the temperature of the assembly was allowed to rise to 155°C. It was then inserted into a cooling press. A TMA of the resulting material gave transitions or softening points at 45°C and 123°C as well as the T_g at 243°C. A good film was not formed however, because of excessive flow.

A visual study of resin 1885's flow characteristics was then made. A sample of the original resin was placed on the room temperature, Fisher-Johns melting-point block. The block was then heated rapidly to 150°C. The sample began to coalesce at 105°C, and by 145°C it was a true low viscosity melt.

To determine whether a continuous film can be made with the low viscosity melt, a sample of resin and 0.006 in. shims were placed between sheets of Frekoted Kapton. The assembly was placed in a 149°C press for 10 seconds and then removed and allowed to cool.

The resulting film had many small pin holes and was a slightly darker color than the original material. A TMA of this material gave only a softening point beginning at 35°C and a T_g at 253°C. The resin began to coalesce on the melting-point block at 35°C and became a true melt by 55°C.

The film was broken up, pushed into a pile and pressed again at 38°C. This produced a very small but even film of uncured resin. (A summary of the TMA, DSC, and melting-point block data is given in Table 11.) This work was repeated with a slightly larger sample, and this again produced a good quality film. We used this film to establish preliminary cure conditions for this resin.

The following conditions were used to produce the form of resin 1885 with a T_g of 35°C:

- A pile of as-received resin was placed between sheets of Frekoted Kapton with 0.15-mm shims.
- The assembly was placed in a 300°F press until the resin melted.
- A caul was placed on top and lowered to the 0.15-mm shims.
- The assembly was removed from the press and cooled.
- The resulting resin had a T_g of 35°C.

Table 11

SUMMARY OF DSC, TMA, AND MELTING-POINT BLOCK DATA FOR RESIN 1885

	DSC	TMA	Melting Block
Original resin (1885) Prior to heat treatment	Melt point 162°C Polymerization: Onset 170°C Peak 231°C	--	--
After heat treating to 175°C and rapid cooling	T_g = 27°C Slight exotherm at 95°C T_m = 140°C, 155°C	--	--
After heat treating to 175°C and slow cooling	T_g = 28°C		
Resin 1885 received by SRI Prior to heat treatment	--	Mobile 50°C-150°C T_g = 243°C	Spots of coalescence form 35°-45°C but disappear; coalescence begins again at 105°C and continues to melt at ~145°C
After heating to 155°C and rapid cooling with vacuum bag	--	Transitions at: 45°C 123°C 243°C	--
After heating to 149°C and cooling (no vacuum bag)	--	T_g = 35°C Minor T_g = 253°C	Coalescence begins at 35°C and melt at 55°C

Our major concern in establishing a cure for the film formed at 38°C (above) was the retention of the quality of the film. The following cure cycle was used:

- Film remained between sheets of Frekoted Kapton, and the 0.15-mm spacers were retained.
- Hold at 38°C 2-1/2 hrs.
- Heat to 66°C; hold 15 min.
- Heat to 93°C; hold 45 min.

The film was inspected at 15- to 30-min intervals. Gradually the original film became powdery and there were no visible signs of cure. The resin was then heated to 232°C and held one hour. The resulting film (2663-9) exhibited considerable flow despite a complete lack of pressure. In addition, there were multiple pin holes in the region of the original film, but not in the areas that were a result of flow.

From this work, several observations were made: (1) the form of the resin with a T_g of 35°C is not preferred (given time and temperature, it reverts to the higher melting forms), (2) one hour at 232°C is sufficient to cure this resin, and (3) the low melt viscosity and pin holes must be taken into account when determining process parameters.

We then began a series of experiments to help define the parameters necessary for cure and those necessary to control the flow and eliminate the pin holes.

The time and temperature necessary for cure were better defined by dropping resin onto a hot Fisher-Johns melting point block and monitoring the mobility. Three temperatures were used: 170°C, 195°C, and 235°C, where the low and high temperatures correspond to the onset of polymerization and the peak of polymerization given by DSC data provided by AFML. There was no evidence of cure at 170°C, after 8 min, nor after 5 min at 105°C; cure to immobility was effected in approximately 5 min at 235°C. At all three temperatures, the viscosity of the melted resin was very low.

Because cure is not rapid at a temperature just above 162°C (the highest melting point observed for this resin), a reasonably large processing window exists. The remainder of the experiments completed during this report period exploited the processing window in attempts to control flow and to eliminate the pin holes.

The following pair of experiments were based on the observation of the very low viscosity melt of resin 1885. In both experiments a 0.15-mm high sealant dam (circular) was made on a piece of Frekoted Kapton. In the first experiment, resin was piled in the cavity; in the second, the resin was distributed evenly in the cavity. Both assemblies were placed on 170°C platen until melting occurred (~10 sec), after which assemblies were cooled and inspected. Both films were thickest in the center and

tapered towards the edges. The thickness of the first film was 0.027 in. and the second was 0.016 in. thick.

In the next experiment a 0.15-mm-thick sealant dam was prepared on a piece of Frekoted Kapton. Resin was spread evenly in the cavity. The assembly was inserted into a 170°C press until the resin melted; then a caul plate wrapped in Frekoted Kapton was laid onto the shims. The assembly was heated one hour at 170°C and then cooled slowly. The resulting film was smooth and even, but contained numerous pin holes..

The final and successful experiment performed during this report period produced a small (6-mm-diameter) film, that was smooth, even, and without pin holes. A 0.15-mm-thick sealant dam was made on a piece of Frekoted Kapton; resin was placed inside the dam. The assembly was then placed in a 170°C press. A Kapton-covered caul was placed on top of the melted resin (~10 sec) and the whole assembly was removed from the press and cooled. The uncured resin film was even, but had numerous pin holes. The bottom piece of Kapton with the sealant dam and resin film were placed in a vacuum oven that was preheated to 170°C. The temperature and full vacuum were held at 45 min and then the film was cooled slowly under vacuum. Though the film did not appear completely cured, the pin holes that were previously present were undetectable. The cure was completed by reinserting the dam-Kapton-resin assembly into the 170°C vacuum oven, reapplying the vacuum, and curing an additional 5 hrs. The resulting film remained smooth, even, and free of pin holes, and it was considerably darker in color. Its thickness was 0.18 mm and a TMA showed a T_g at 250°C and almost no mobility.

We used this procedure to prepare a 16 x 100 mm film. A 0.15-mm dam was prepared on a piece of Frekoted Kapton and resin was distributed in the cavity. This was a difficult procedure due to the electrostatic attraction of the resin. The assembly was then placed in a 170°C press. When the resin melted, a caul covered with Frekoted Kapton was used to press the resin down to 0.15-mm shims, and the assembly was removed from the press. Some areas of the resulting film were not completely filled and other areas had overflowed the cavity. We then placed additional resin into the cavity and repressed the film at 170°C, but this film also did not fill the cavity. We observed that once resin overflowed the cavity, additional resin tended to overflow rather than fill the cavity.

We then made another sealant dam and placed the resin (from above) into the cavity. It was pressed into a good quality film without allowing the resin to overflow the cavity. The Kapton-dam-resin assembly was then cured by placing it in a 170°C vacuum oven for 5-3/4 hrs.

The surface of the resulting film showed evidences of breaking bubbles. Although there was mobility left in the resin when the cure began, it was insufficient to allow the resin to form a smooth film. This can probably be attributed to the multiple exposures to 170°C before beginning the cure. The film and Kapton adhering to it were both curved about the longitudinal axis of the film.

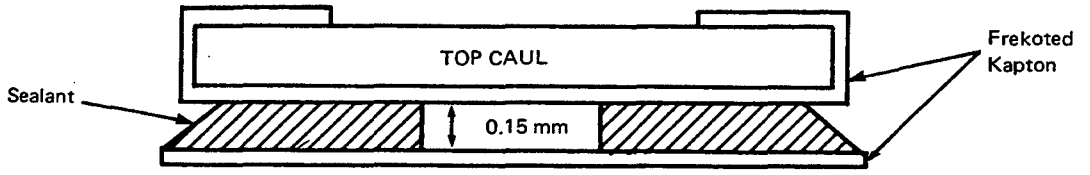
In addition, the color of the film was not uniform; it appeared mottled, ranging from amber to nearly black.

The problem observed during the above experiment can be summarized as follows:

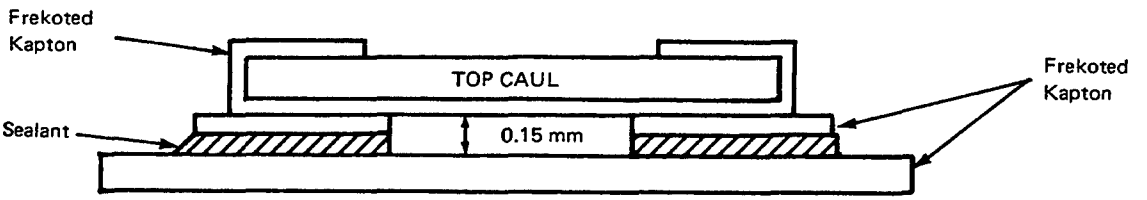
- The hard resin appears to have a high electrostatic charge and is difficult to handle.
- Once a portion of resin overflows the cavity, resin tends to overflow the cavity in large amounts.
- The cured resin is difficult to remove from separator films without cracking.
- Multiple exposures to 170°C and higher temperatures result in excessive staging and reduced mobility.

In devising solutions to the problems, we first tried a variety of spatulas and found that a ceramic spatula was least affected by the static electricity.

We next designed a slightly different cavity assembly, as shown in Figure 5. The processing was altered so that only the first pressing of the resin was at 170°C and all subsequent pressing was performed at 38°C. (The T_g of the resin after one exposure to 170°C is 35°C.)



Cross-section of the Original Film Forming Assembly for Resin 1885



Cross-section of the Revised Film Forming Assembly for Resin 1885

Figure 5 Cavity Assembly

Using the revised assembly, we placed resin in a 30 x 16 mm cavity, placed it into a 170°C press, allowed the resin to melt, and then pressed it into a film. There was overflow in some areas and insufficient resin in others. The overflow was scraped from the Kapton and placed in the cavity, and additional resin was added as needed. The resin was again pressed, this time at 38°C to provide a smooth, even film that filled the cavity. The assembly and resin film were taped to a caul and inserted into a 170°C vacuum oven. After two hours, the film was removed and examined.

The assembly had warped away from the caul, causing the resin to flow to one corner. A 0.04-mm-thick film was left over the rest of the bottom of the cavity, and the film was too thin to remove without breaking. There were also some small dark bits of resin in the bottom of the cavity that evidently did not melt but formed small lumps in the 0.04-mm-thick film. All these resin bits were less than 0.13 mm and would not preclude a smooth surface on a thicker film. The warpage was prevented by attaching the assembly to a rigid backing and then checking the assembly for warpage during a cure cycle.

We used the previously developed processing schedule and fabricated a 16 x 30 mm film and three 15 x 100 films (nominal dimensions) from unwarped cavity assemblies. One of the larger films broke while handling. All of the films were sent to AFML for evaluation.

We were then asked by AFML to fabricate additional thin films of resin 1885 that would be transluscent enough for infrared analysis. A nominal thickness of 0.025 to 0.050 mm was chosen as being thin enough to transmit light.

A 5 x 5 x 0.05 mm cavity was prepared. Resin was pressed into the cavity at 170°C. (No additional pressing was necessary to fill the cavity.) The film was cured 5 hours at 170°C in a vacuum oven. The resulting film was 0.038 mm thick in the center and 0.1 x 3 to 0.1 x 5 mm thick at the edges. Using an attenuator on a Perkin-Elmer 281 Infrared Spectrometer, an IR spectrum was obtained.

Using the same procedure as above, a 15 x 35 mm film was fabricated. The film was 0.13 mm thick and had several holes. It appeared as though the surface tension of the melted resin caused puddling rather than retaining the even distribution of the resin.

An IR analysis of this film was obtained indicating that 0.13 mm is a satisfactory thickness. This work will be continued.

D. RPS/P1700 Matrix Resin

1. ATS as a Reactive Plasticizer (RPS) for P1700

Work in the past year[9] with a 1:4 w/w ratio of RPS to P1700 was somewhat disappointing. Although the T_g of the mix was slightly higher

than that of pure of P1700, we observed little improvement in elevated temperature composite properties and only a minor improvement in solvent resistance.

We decided, therefore, to further test the RPS approach by

(1) Increasing the level of RPS to a 1:1 ratio

(2) Evaluating the effects of extended high temperature curing on both the 1:4 and 1:1 mixes.

A 36 wt percent solids solution was prepared using 1:1 w/w RPS-P1700 in methylene chloride. This solution was prepregged onto AS fiber using the following parameters, developed earlier for the 1:4 RPS-P1700 solution:

No pot heaters
Banding rolls 380°C
0.159 cm (0.0625 in.) orifice
Slow to medium take-up speed.

The prepreg was smooth, even, and easily heat tacked. However, the resin content was only 28 to 30 percent.

A TMA profile as a function of cure history was taken of this prepreg (see Table 12).

A Small laminate $|0°|_2$, (3.8 cm by 1 cm), was made after bringing the resisn content of the prepreg up to 39 percent. The cure and postcure schedules are shown in Table 13.

No evidence of warpage was observed following the unrestrained postcure. The resin content of the laminate was 30 percent and the specific gravity was 1.62. This sample was examined by TMA before and after the postcure. Before postcure, triplicate TMA trials showed softening beginning at about 190°C and ending at about 250°C. After postcure, the TMA showed only traces of softening in the sample, indicating that significant additional curing had occurred.

A laminate large enough for mechanical property testing was made in the same manner. No warpage was observed during postcure. The TMA of this laminate showed a sharp T_g peak at 216°C, indicating incomplete cure. This was unexpected. The laminate was postcured for two more hours at 316°C. A TMA trace showed that the peak had disappeared, indicating that the cure was now complete. Table 14 summarizes the properties of the laminate (No. 2349-27).

The laminate showed increased solvent resistance and elevated temperature performance, which encouraged a further look at the 1:4 RPS-P1700 mix. Old specimens were examined by TMA; curves indicated incomplete cures for all samples. Several of these pieces were then

Table 12

TMA PROFILE OF RPS-P1700 1:1/AS PREPREG

Cure	Location of TMA Peaks
1/2 hr at 93°C	Started softening immediately
+ 4 hrs at 177°C	173-182°C
+ 1 hr at 260°C	200-227°C
+ overnight at 288°C	217°C
1 hr at 204°C	191°C
2 hrs at 204°C	191°C, 200-230°C
4 hrs at 204°C	200-230°C

Table 13

CONDITIONS OF CURE AND POSTCURE FOR RPS-P1700 1:1 LAMINATE

Bag	Cure	Postcure
Kapton bag 1 ply 181 glass caul 1 ply 181 glass 2 plies Armalon Layup 2 plies Armalon 1 ply 181 glass base caul	Heat to 204°C, full vacuum, 1.4 MPa pressure (200 psi), hold 4 hrs, cool	Overnight in an air-circulating oven at 288° unrestrained

Table 14

PROPERTIES OF LAMINATE 2349-27
(Resin Content by Digest, 28.0 percent
Specific Gravity, 1.61)

Sample	Test Temperature	Short Beam Shear Strength
-1	RT	67.6 MPa (9,800 psi)
-2	177°C	46.9 MPa (6,810 psi)
-3	177°C	43.0 MPa (6,240 psi)

Solvent resistance

$CHCl_3$, no visible effect

MEK, no visible effect

Toluene, no visible effect

THF, slightly swollen

postcured for 2 to 3 hr at 316°C. We tested them and found a dramatic improvement in solvent resistance and a reduction of the TMA peak.

New work was then initiated on the 1:4 RPS-P1700 system. A solution was prepregged onto AS fiber and a $|0°|_2$ (10 cm by 5 cm) panel was laid up. The panel was cured according to the schedule in Table 14 and postcured 3 hr at 316°C. Dry fibers were present in this laminate both before and after the postcure and the specific gravity was only 1.48 despite a resin content of 36 percent. In addition, the ambient short beam shear strength tests showed that the specimens averaged only 50.6 MPa (7,340 psi). Further testing of this laminate was abandoned due to the evidently poor quality of the laminate.

We reviewed the laboratory notebooks to determine if any changes in the processing procedure might account for the poor wetting observed in recent laminates. We found that the prepreg used for all the laminates had a low initial resins content. Additional resin had been added to earlier laminated by applying a dilute resin solution (2 to 6 wt percent solids) of low viscosity to the tows. The more recent laminates that exhibited dry fibers had been prepared from tows that were given an additional coat of viscous, 25 to 30 wt percent solids resin solution. The viscous solutions evidently had not penetrated the resin-poor tows of prepreg, leaving resin-starved areas in the fibers. Suprisingly, subsequent resin flow during processing was not enough to correct these defects in the prepreg.

Even though the small (2.5 cm by 2.5 cm) laminate was flawed by dry fibers, short beam shear strength values were 60.5 MPa (8770 psi) at room temperature and 37.6 MPa (5450 psi) at 177°c). The solvent resistance was evaluated and proved to be significantly better than that of previous panels. This is attributed to a higher degree of cure in the panel. Table 15 summarizes the solvent tests.

Table 15

EFFECTS OF SOLVENTS ON WELL CURED LAMINATE
1:4 RPS-P1700

Solvent	Effect
MEK	24 hr no effect
Toluene	24 hr no effect
Chloroform	24 hr mild swelling
THF	24 hr mild swelling

We believed that a full cure might improve both moisture resistance and solvent resistance. The larger panel, 5 cm by 10 cm, which we had discontinued testing because of dry fibers, was retrieved and short beam shear specimens were cut. We subjected them to environmental aging (71°C, 95 percent RH) to pseudosaturation, and tested them at room temperature and 177°C. Our objective was to compare the thermoplastic failures modes of incompletely cured specimens with those of well-cured shear specimens.

Table 16 compares the results of early environmentally aged samples with the well cured, flawed, panel. The more complete cure and postcure significantly improved the performance of the 1:4 RPS-P1700 resin system.

New prepreg was prepared, taking care to achieve good fiber wet-out. A new laminate, $[0°]_7$, 5 cm by 7.5 cm, was fabricated. Unfortunately, we had a bag failure during cure, after six hours at 204°C, but the laminate appeared to be sound. However, some localized delimination occurred during postcure, perhaps a result of entrapped solvent. The laminate showed no dry fibers, and had a specific gravity of 1.47 and a resin solids content of 36.6 wt percent.

This well-cured laminate performed significantly better than previous P1700/AS laminates and 1:4 RPS-P1700/AS laminates with lower degrees of cure. We checked moisture pickup, solvent resistance, and short beam shear strength of the laminate at ambient and elevated temperatures before and after environmental aging. Tables 17, 18 and 19 present the data for

Table 16

ENVIRONMENTAL AGING COMPARISON OF 1:4 RPS-P1700/AS PANNELS

Panel	State	Test Temperature	Short Beam Shear Strength, MPA (psi)	Comments
Well-cured, flawed	Control	Ambient	51.0 (7340)	Sharp failure
		149°C	39.1 (5630)	Slightly thermoplastic
		177°C	29.3 (4220)	Slightly thermoplastic
	Aged	Ambient	44.0 (6330)	Sharp failure
		149°C	29.6 (4260)	Slightly thermoplastic
		177°C	15.9 (2290)	Thermoplastic yield
Lower state of cure, not flawed	Control	Ambient	88.2 (12700)	Sharp failure
		149°C	39.7 (5720)	Thermoplastic yield
		177°C	16.2 (2330)	Thermoplastic yield
	Aged	Ambient	72.9 (10500)	Sharp failure
		149°C	27.5 (3960)	Thermoplastic yield
		177°C	7.3 (1050)	Thermoplastic yield

Table 17

ENVIRONMENTAL AGING DATA OF
1:4 RPS-P1700/AS LAMINATE (2349-43)

Test Specimen	Test Temp.°C	Short Beam Shear Strength* MPa (Psi)	Percent Retention After Aging
Control	RT	67.8 (9840 psi)	
	149	44.8 (6500 psi)	
	177	32.4 (4700 psi)	
Specimen aged at 160°F/95% RH	RT	55.5 (8050 psi)	82
	149	36.2 (5250 psi)	81
	177	20.6 (2990 psi)	64

*Average of three specimens tested.

Table 18

MOISTURE ABSORPTION OF
1:4 RPS-P1700/AS LAMINATE (2349-43)

	Hours			
Sample No.	0	48	72	144
22	0%	.41%	.59%	.44%
23	0%	.41%	.44%	.46%
24	0%	.355%	.38%	143%

Table 19

QUALITATIVE SOLVENT RESISTANCE OF
1:4 RPS-P1700/AS LAMINATE (2349-43) AT AMBIENT TEMPERATURE

Solvent	Effect After 24 Hours	Effect After 72 Hours
Methyl ethyl ketone	No effect	Slight swelling
Toluene	No effect	Slight swelling
Chloroform	Slight swelling	Slight swelling and very slight dissolution
Tetrahydrofuran	Slight swelling	Slight swelling and very slight dissolution

these tests. The laminate showed reduced moisture pickup, improved solvent resistance, and higher short beam shear strengths at 350°F, both before and after environmental exposures.

These results clearly demonstrate the feasibility of the reactive plasticizer concept. It should be noted that longer postcures and higher postcure temperatures are needed as the amount of RPS is decreased. Table 20 summarizes the cure/postcure characteristics of RPS/P1700 blends.

2. P1700 as a Toughener for ATS

We next began to investigate the matrix 80 percent ATS, 20 percent P1700, i.e., P1700 as a toughener for ATS.

We first made a 55.5 percent ATS P1700 (4:1 w/w) methylene chloride solution. The solution was prepregged onto unsized Celion 6000 under the following conditions:

- No leak in post or banding rolls
- ~15 cm/min take up speed
- 1.6 mm orifice.

The resulting prepreg appeared to be well wet-out and had a resin content of 65 percent. This was much higher than we desired, but because we lacked ATS, we continued our study with the resin-rich prepreg.

We then established a TMA profile for the resin as a function of cure history, as we had for ATS-1700(1:4) and ATS-P1700(1:1). The results are presented in Table 21. They indicate that the conditions necessary for curing the ATS-P1700(4:1) matrix are midler than those necessary for curing the ATS-P1700(1:1) matrix. These results follow the general trend observed in other cures, i.e., that the higher the percentage of ATS, the milder the processing conditions (see Table 22). In effect, the P1700 dilutes the ATS and interferes with curing.

After the TMA study, we ran a flow test. Five minilayups were made (1 tow wide x 3.8 cm long, $[0]^\circ_2$), Each laminate was staged at 177°C for 0 15, 30, 45, and 60 minutes, respectively. They were then vacuum bagged:

- Kapton bag
- 2 plies 181 glass
- top caul plate
- 2 plies 181 glass
- 1 ply Armalon
- layups

Table 20

CURE CHARACTERISTICS OF RPS/P1700 BLENDS

100% RPS/ 0% P1700	50% RPS/ 50% P1700	20% RPS/ 80% P1700	0% RPS/ 100% P1700
After 4 hours at 177°C, a laminate can be postcured at 282°C without warpage.	After 4 hours at 177°C, a laminate will warp when postcured at 282°C After 4 hours at 204°C, a laminate will not warp when postcured at 282°C.	After 4 hours at 177°C, a laminate will warp under postcure. After 20+ hours at 204°C, a laminate will not warp when postcured at 282°C.	T_g = 190°C Requires processing at 314°C and will not "cure" at that temperature.

Table 21

TMA PROFILE OF RPS-P1700 4:1 PREPREG
AS A FUNCTION OF CURE

Heat History	TMA Peaks
Unheated prepreg	started softening immediately
30 min at 177°C	48° - 76°C
1 hr at 177°C	70° - 112°C
2 hr at 177°C	80° - 142°C
30 min at 204°C	117° - 161°C
1 hr at 204°C	170° - 227°C
2 hr at 204°C	185° - 250°C
3 hr at 204°C	200° - 270°C
4 hr at 204°C	200° - 270°C*

*Nominal values only; practically no movement was observed.

- 1 ply Armalon
- 2 plies 181 glass
- base caul.

The vacuum bagged laminates are then cured:

- Apply vacuum, 1.4 MPa, and place in RT press
- Heat to 204°C
- Hold 4 hours
- Cool Slowly.

The amount of flow was noted for each sample (see Table 23). We selected 30 minutes as the staging time because a sample staged for this period, the longest tested, still flowed evenly.

A laminate (2.8 cm wide x 4.1 cm long, $[0]_{12}$) was laid up with the remaining prepreg, solvent tacked together, vacuum bagged,* cured,* and

*Vacuum bag and cure conditions are the same as those used for the flow test.

Table 22

CURE CHARACTERISTICS OF ATS/P1700 BLENDS

100% ATS/0% P1700	80% ATS/20% P1700	50% ATS/50% P1700	20% ATS/80% P1700	0% ATS/100% P1700
After 4 hours at 177°C, a laminate can be postcured at 282°C without warpage.	After 3 hours at 204°C, a laminate will not warp when postcured at 282°C. After 4 hours at 204°C, practically no mobility remained in the laminate. TMA at that time is similar to ATS/P1700 (1:1) after postcured overnight at 282°C.	After 4 hours at 177°C, a laminate will warp when postcured at 282°C. After 4 hours at 204°C, a laminate will not warp when postcured at 282°C.	After 4 hours at 177°C, a laminate will warp when postcured at 282°C. After 20+ hours at 204°C, a laminate will not warp when postcured at 282°C.	T_g = 190°C Requires processing at 314°C and will not "cure" at that temperature.

Table 23

FLOW TEST OF ATS-P1700 4:1/CELION 6000

Staging Time (min)	Percent Resin	Percent Resin After Staging	Percent Resin After Curing
0	55.0	55.0	31.0
15	62.4	54.6	36.5
30	65.0	53.8	42.5
45	69.0	65.0	57.5
60	54.0	50.5	51.0
60	62.0	57.0	56.0

postcured overnight at 288°C. The resulting laminate did not spread and was 12.7-mm thick. It had a calculated resin content of 33.5 percent and a specific gravity of 1.57. This laminate was cut into short beam shear specimens for aging at 71°C and 95 percent relative humidity. Mechanical property results are given in Table 24 and can be compared with the results of other RPS-P1700 laminates. Moisture absorption characteristics are given in Table 25 and solvent resistance in Table 26.

Table 24 shows that adding 20 percent RPS provides a dramatic improvement over the 100 percent P1700 laminate in all respects except in unaged, room temperature, short beam shear values.

It is also apparent that 100 percent RPS laminates demonstrate better retention of mechanical properties at elevated temperatures, both with and without environmental aging, than do any of the laminates with P1700. This is consistent with what one would predict. We could not draw conclusions as to the optimum blend of the two systems because it would depend on the desired application and is beyond the scope of an evaluation program such as this.

The original goal of this work, to plasticize P1700 for the purpose of processing at temperatures less than or equal to 240°C and 1.4 MPa, was met. All three RPS-P1700 blends conform to these requirements. The amount of time at 240°C required for cure increases as the percentage of P1700 increases.

The concept of reactive plasticizers was demonstrated by the RPS-P1700 system. However, this work has also increased the scope of possibilities available with a two-resin system. In addition to processing, it may be possible to tailor other parameters including solvent resistance, use temperature, mechanical properties, fatigue properties, and stiffness.

Table 24

COMPARISON OF MECHANICAL PROPERTIES OF LAMINATES
WITH RPS-P1700 BLENDS AS MATRIX RESINS

	No Aging	No Aging	No Aging	71°C/ 95% RH	71°C/ 95% RH	71°C/ 95% RH
Test temp. (C°)	RT	149	177	RT	149	177
Laminate 2349-1* 100% P1700, 0% RPS						
MPa	61.8	36.8	23.7	29.8	19.2	11.2
psi	(8960)	(5340)	(3440)	(4320)	(2790)	(1630)
Laminate 2349-43† 80% P1700, 20% RPS						
MPa	67.8	44.8	32.4	44.4	36.2	20.6
psi	(9840)	(6500)	(4700)	(8050)	(5250)	(2990)
Laminate 2349-27‡ 50% P1700, 50% RPS						
MPa	67.6	--	45.0	--	--	--
psi	(9800)		(6525)			
Laminate 2349-89§ 20% P1700, 80% RPS						
MPa	77.2	59.3	46.2	53.1	42.2	32.9
psi	(11,200)	(8600)	(6700)	(7700)	(6120)	(4770)
Laminate 959-34** 0% P1700, 100% RPS						
MPa	59.5	--	56.1	47.3	--	41.4
psi	(8625)		(8130)	(6865)		(6010)

*37.1% resin content by digestion, density of 1.51 g/cc.

†36.6% resin content by digestion, density of 1.47 g/cc.

‡28.0% resin content by digestion, density of 1.61 g/cc.

§33.5% resin content by calculation, density of 1.57 g/cc.

**34.6% resin content by calculation, density of 1.50 g/cc.

Table 25

COMPARISON OF MOISTURE ABSORPTION
OF RPS-P1700 LAMINATES

Hours	Samples			
	100% P1700, 0% RPS 2349-1	80% P1700, 20% RPS 2349-43	20% P1700, 80% RPS 2349-89	0% P1700, 100% RPS
0	0	0		
18	0.78			
24			0.62	0.75
48		0.39		
66	0.94			
72		0.47	0.70	
80				0.83
144		0.44	0.82	0.87
162	1.1			
175				0.87
192			0.89	0.88
217	1.2			
240			0.73	
282	1.2			
330	1.4			
336			0.80	
450	1.4			
477	1.3			

Table 26

COMPARISON OF SOLVENT RESISTANCE OF RPS-P1700 LAMINATES

Solvent	100% P1700, 0% RPS 2349-1	80% P1700, 20% RPS 2349-43		20% P1700, 80% RPS*	100% RPS*
		After 24 hrs	After 4 days		
Methylene chloride	Complete dissolution	Slight swelling	Slight swelling and very slight dissolution	No visible effect	No visible effect
Tetrahydrofuran	Complete dissolution	Slight swelling	Slight swelling and very slight dissolution	No visible effect	No visible effect
Methanol	No visible effect				
Methyl ethyl ketone	Swelling, relaxation, partial dissolution	No effect	Slight swelling	No visible effect	No visible effect
N-Methyl pyrrolidone	Complete dissolution				
Toluene	Swelling, relaxation partial dissolution	No effect	Slight swelling	No visible effect	No visible effect

*These laminates exhibited no change in dimension, but an 0.1-0.2% weight gain after 24 hours in the solvent.

E. Enyne Polysulfones as Matrix Resins

1. Evaluation of Polysulfone, No. 1814

AFML is interested in developing a thermoplastic composite matrix resin with a service temperature of 177°C or more. The leading candidate, a polybiphenyl sulfone, appears to have marginal solvent resistance.

The polymer chemistry group at AFML synthesized and characterized a series of resins and sent us samples of resin No. 1814 for evaluation. This resin is an enyne polysulfone as shown in Figure 6. Resin 1814 may have potential as a solvent resistance substitute for the biphenylsulfone or as a reactive plasticizer for use with the material.

The AFML reported the material to be light sensitive (exposure to light drastically reduced the solubility in common solvents), so appropriate precautions were taken. AFML data on the DSC (20°C)/min heating rate) indicated a softening of the uncured resin at 206°C, polymerization onset at 257°C, and a peak of polymerization at 357°C.

We made up a solution of 20 wt percent No. 1814 in methylene chloride, which gave a suitable viscosity for prepreggging. We coated the solution onto unsized Celion 6000 prepreg, using our Goldsworthy prepregger. Pot and banding rolls were at room temperature. We used a 1.9-mm-diameter orifice, very slow take-up speed (~13 cm/min), and a 20 percent wt solution of No. 1814 in $MeCl_2$.

The resulting prepreg was smooth, even, and stiff with a resin content of 35 wt percent. The tow was not completely wet out by this process, and some dry center fibers could be found by cutting and examining the tow. We used this tow to establish preliminary processing parameters.

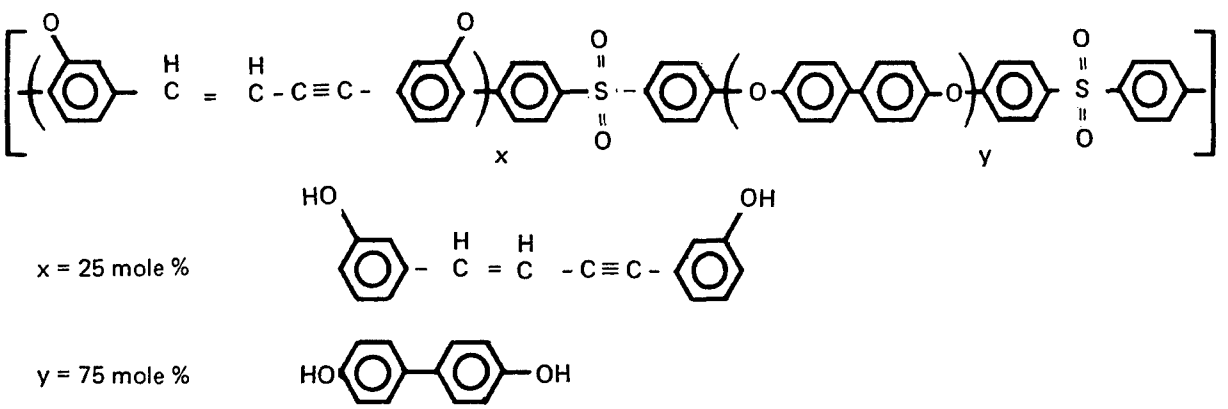


Figure 6 Enyne Polysulfone

A small unidirectional, 4-ply lamainate, 2.5 cm by 1 cm, was heat-tacked together, vacuum bagged, and cured as follows:

Assembly	Cure
Vacuum bag (Kapton)	Place assembly in press
2 plies 181 glass	Apply vacuum and 1.38 MPa
Caul plate	Heat press to 316°C (10°/min)
1 ply 181 glass	Hold 2 hours
1 ply Armalon layup	Cool under pressure
1 ply Armalon	
1 ply 181 glass	
base caul	

The flow was quite low and the wetting was insufficient to wet out the dry fiber found after the prepregging operation. The small amount of remaining prepreg was used to lay up an identical laminate. It was cured by placing it directly into the hot press and increasing the pressure. Both measures were aimed at increasing the flow and wet-out. The following is the cure schedule.

Cure:

Heat press to 316°C

Place assembly in press and apply vacuum and 3.44 MPa

Hold two hours

Cool under pressure

The second minilaminate showed improved wet-out and flow, but was still unsatisfactory.

To achieve better resin penetration, we used a 15 wt percent prepregging solution instead of a 20 wt percent solution. We also spread the fiber out as it entered the pot, and the wet resin was further worked into the fiber with a spatula as the fiber passed over the banding rolls.

The resulting prepreg was 45 wt percent resin and was well wet-out. There was no visual evidence of dry fibers. The tows were smooth and tackfree, but the width of the tows varied.

We made a mini-laminate from this well wet-out prepreg. The mini-laminate was laid up (2.5 cm long x 1.23 cm wide x $[0°]_4$), tacked together with solvent, and cured in a vacuum bag. Table 27 shows the assembly and cure schedule used. This laminate was better quality than previous laminates, but it has a somewhat uneven surface. An examination of cut

Table 27

VACUUM BAG ASSEMBLY AND CURE SCHEDULE
FOR 1814/CELION 6000

Vacuum Bag Assembly

Vacuum bag (Kapton)

2 plies 181 glass

Caul plate

1 ply 181 glass

1 ply Armalon

layup

1 ply Armalon

1 ply 181 glass

Base caul

Cure Schedule

Heat press to 316°C

Apply vacuum

Place vacuum bag assembly in press

Apply 6.2 MPa (900 psi) of pressure

Maintain 2 hr at 316°C

Cool slowly under vacuum and pressure

edges revealed no dry fibers. The laminate was 0.5-mm thick and had spread sideways from 1.23 cm to 1.6 cm. The specific gravity of this laminate was 1.45 g/cc and it had a calculated resin content of 49 wt percent. A portion of this laminate was placed in Skydrol. There was no visual evidence of swelling or dissolution.

A second mini-laminate was laid up (2.5 cm long x 1.9 cm wide x $[0°]_{10}$). The vacuum bag assembly and cure schedule are given in Table 28.

The resultant laminate was of good appearance and showed no dry fibers. It had a specific gravity of 1.47 g/cc and a calculated resin content of 50 wt percent. The laminate lost 5.8 percent of its weight during cure. Short beam shear values for two specimens cut from this laminate were 59.7 MPa (8660 psi) and 63.8 MPa (9250 psi), respectively. These values are high enough to evaluate the solvent resistance of resin 1814 as compared to Radel.

Additional prepreg was made according to the conditions described earlier in this report. Another laminate was laid up (5.4 cm long x 2.2 cm wide x $[0°]_{10}$), vacuum bagged,* and cured (as in Table 7). The appearance of this laminate was good. The calculated resin content was 53.5 wt percent and the specific gravity was 1.45 g/cc. We cut 12 short beam shear specimens from this specimen. Four were aged under ambient conditions for 28 days, four in Skydrol at 160°F for 28 days, and four at room temperature in methyl ethyl ketone for 28 days. Two specimens from each category were tested at room temperature and two at 177°C. All specimens were weighed and measured before aging.

2. Reference Radel/Celion 6000 Laminate

To compare the solvent resistance of Radel to Resin 1814, we prepared Radel/Celion 6000 prepreg according to the procedures developed for 1814. The prepreg was then dried at 204°C for 1.5 hrs. (The Radel was dissolved in N-methyl pyrrolidone rather than methylene chloride.) From this prepreg, a laminate (3.8 cm wide x 4.7 cm long, $[0]°_5$) was laid up, heat tacked together, and consolidated at 343°C for 15 min. The resulting laminate had a calculated resin content of 45.8 percent and a specific gravity of 1.51. Short beam shear specimens were cut from this laminate. As was done for resin 1814, four specimens were aged under ambient conditions, four in Skydrol at 71°C, and four in MEK at room temperature. The results of aging of the Radel and the 1814 matrix laminates are given in Table 29.

The level of reactivity in 1814 appears to provide excellent Skydrol resistance; a lower level would be worth investigating.

Table 28

FINAL CONDITIONS FOR VACUUM BAG ASSEMBLY AND CURE SCHEDULE FOR 1814/CELION 6000*

Vacuum Bag Assembly

Vacuum bag (Kapton)

2 plies 181 glass

Caul plate

1 ply 181 glass

Layup wrapped twice around with Armalon†

1 ply 181 glass

Base caul

Cure Schedule

Heat press to 316°C

Apply vacuum

Place vacuum bag assembly in press

Apply 6.9 MPa (1000 psi) of pressure

Maintain 2 hr at 316°C

Cool slowly under vacuum and pressure

*The conditions in Table 6 differ only in the amount of Armalon in the vacuum bag assembly and the amount of pressure applied during cure.

†To contain sideways flow.

Table 29

SOLVENT RESISTANCE, CELION 6000 REINFORCED 1814 VS. RADEL

Specimen	Test Temp.	Weight Gain (%)	Dimensional Change (%)	Short Beam Shear MPa	Short Beam Shear (psi)	Average Retention (%)
Controls						
1814	RT	--	--	68.3	(9900)	--
				66.9	(9700)	
	177°C	--	--	39.0	(5650)	--
				40.1	(5820)	
Radel	RT	--	--	63.8	(9250)	--
				67.2	(9750)	
	177°C	--	--	40.4	(5860)	--
				37.4	(5420)	
Warm Skydrol Soak*						
1814	RT	0.53	--	64.8	(9400)	99
		0.46		68.9	(10,000)	
	177°C	0.67	--	38.3	(5550)	98
		0.64	--	39.3	(5700)	
Radel	RT	0.25	--	68.7	(9960)	101
		0.60	1.0	63.1	(9150)	
	177°C	0.48	0.2	35.6	(5160)	90
		0.51	0.8	34.7	(5030)	
MEK Soak†						
1814	RT	5.6	~3	63.4	(9200)	83
		6.5	0.5	48.3	(7000)	
	177°C	5.7	0.5	31.0	(4500)	63
		8.0	1.5	18.6	(2700)	
Radel	RT	11.8	0.8	26.0	(3700)	40
		11.5	0.8	27.0	(3920)	
	177°C	10.5	1.4	24.3	(3530)	60
		10.2	2.0	22.7	(3290)	

*Aged 28 days at 71°C.

†Aged 28 days at room temperature.

Methyl ethyl ketone (MEK) proved to be a harsh environment for both materials. The 1814/Celion 6000 panel demonstrated considerably better room temperature mechanical properties after aging to MEK (55.9 MPa as compared with 26.5 MPa), but properties of the panels at 177°C after aging in MEK were comparable (24.8 MPa and 23.5 MPa) and failures were thermoplastic. In general, the failures of unaged specimens were sharper than the failures of Skydrol-aged specimens which in turn were sharper than the failures of MEK-aged specimens. The exceptions were those 1814/Celion 6000 specimens that were aged in Skydrol and tested at room temperature; they had the sharpest failures of all.

If resistance to prolonged MEK exposure is required, a higher level of reactivity than that of 1814 will be required to achieve improved resistance to the solvent.

3. Evaluation of Polysulfone BR-2-17

After reviewing the evaluation of Radel and Resin 1814 as composite matrix materials, the polymer chemistry group of AFML sent us a second candidate resin to evaluate (BR-2-17). BR-2-17 is similar to resin 1814 except that in resin 1814 X = 25 mole percent and Y = 75 mole percent.

Using appropriate precautions for a light-sensitive resin, we dissolved 3.39 g in dichloromethane to make a 20 wt percent solution. The viscosity of this solution seemed appropriate for prepregging. After sitting for 48 hours at room temperature, the solution became a white, pastelike substance. Little or no solvent had evaporated from the solution. Additional solvent was added to make the solution 15 wt percent solids. This produced a white suspension of a viscosity suitable for prepregging. However, we decided to use a fresh solution to avoid possible difficulties in flow and wet-out due to the suspension.

We then made a 24 percent solution of the BR-2-17 and prepregged it immediately onto unsized Celion 6000. Conditions were as follows:

- 0.073-in orifice
- No heat in pot or banding rolls
- Speed ~5 in./min
- The tow was spread before it entered the pot and the resin was further worked into the fiber with a spatula as the prepreg was passed over the banding rolls.*

These conditions produced prepreg that appeared well wet-out and had a high resin content (54.6 percent by weight). This prepreg was satisfactory

*Conditions were the same as for prepregging 1814.

for our initial process development. It was characterized and results are given in Table 30.

We then laid up an 8 mm x 20 mm $[0]_6$ mini-laminate. The tows were tacked together with methylene chloride, and the plies were tacked together in a similar manner.

The layup was double-wrapped in Aramlon to prevent sideways flow and was vacuum-bagged as follows:

Kapton bag
2 plies 181 glass
top caul
1 ply Kapton
2 plies 181 glass
1 ply Armalon
Armalon-wrapped layup
1 ply Armalon
2 plies 181 glass
1 ply Kapton
Base caul.

Based on the TMA data, the laminate was cured according to the following schedule:

- Apply full vacuum
- Place vacuum bag assembly in 250°C press
- Apply 3.3 MPa
- Hold at 250°C for 1-1/4 hrs
- Hold at 350°C (~45 min)
- Hold 2 hrs
- Cool slowly under vacuum and pressure.

The resulting laminate had a calculated resin content of 58.5 percent and a volatiles content of 5.7 percent; it exhibited no bleed. The laminate was badly tapered, however, due to a shifting of the top caul. The laminate appeared well consolidated when it was sectioned and examined.

A TMA of this laminate gave a T_g of 239°C and showed that decomposition begins at 350°C (in air). The prepreg indicated that the T_g after two hours at 350°C should be 285°C.

We recured the wedge-shaped mini-laminate to raise the softening point. After the mini-laminate was held for two additional hrs at 350°C, the T_g remained essentially unchanged at 243°C.

Another mini-laminate was fabricated from this resin to determine preliminary mechanical properties. The layup was wrapped in Armalon, vacuum-bagged as described previously, and cured as follows:

Table 30

TMA PROFILE OF BR-2-17/CELION 6000 PREPREG

Sequence of Steps	Material Form	TMA Peaks	Comments
1	Raw prepreg	15-140°C and 145°-300°C	Two distinct changes
2	After 1/2 hr at 93°C and room temperature for several days	60-315°C	Two distinct changes
3	1-1/2 hr at 93°C	110-300°C	One major broad section of mobility
4	1 hr at 93°C	120-305°C	One major broad section of mobility
5	1 hr at 200°C	150-300°C	One major broad section of mobility
6	1-1/4 hr at 250°C	T_g = 220°C	
7	1 hr at 300°C	T_g = 225°C	
8	1-1/4 hr at 350°C	T_g = 270°C	
9	2 hr at 350°C	T_g = 285°C	
10	4 hr at 350°C	T_g = 380°C	Signs of decomposition

- Apply full vacuum
- Place vacuum bag assembly in 250°C press
- Apply 6.9 MPa
- Hold at 250°C for 1-1/4 hrs
- Hold to 350°C (~45 min)
- Hold 2 hrs
- Cool slowly under vacuum and pressure.

The resulting laminate lost 6.3 percent volatiles; it was smooth and even and gave a clear C scan. It had a density of 1.53 g/cc, a resin content of 42.2 percent, and a T_g of 238°C. The resin temperature short-beam shear values obtained--89.2 MPa and 83.4 MPa--are high enough to justify an investigation of this resin's solvent resistance. Accordingly, we dissolved the remainder of the BR-2-17 resin in dichloromethane (24 percent solution) and prepregged it onto Celion 6000, using the procedure previously described.

A $[0°]_{10}$, 2.5 cm x 5 cm laminate was laid up from this prepreg and cured according to the procedure described above. The resulting laminate had a good appearance and a clear C scan (Figure 7). It also had a density of 1.53 g/cc, a T_g of 243°C, and a resin content of 43.2 percent. The average room temperature short-beam value was 75.2 MPa. The laminate was machined into short-beam shear specimens. Half were aged under ambient conditions and half were aged in Skydrol at 71°C until the pseudosaturation point was reached.

Skydrol-aged specimens gained an average of 0.3 wt percent and the average dimensional change was +0.6 percent. The average short-beam shear strength at room temperature was 74.05 MPa without aging and 74.08 MPa after aging in Skydrol. At 177°C, the average short-beam shear strength was 51.2 MPa without aging and 51.9 MPa after aging in Skydrol. The results are shown in Table 31 and indicate that the Skydrol has little, if any, effect on the shear strength of BR-2-17 laminates.

4. Evaluation of BR-2-22 Resin

A DSC of the resin showed a T_g at 200°C, a polymerization onset at 255°C, and a polymerization peak at 342°C. This DSC sample, which had been heated to 450°C, was then cured for 6 hours at 343°C. The resin then had a T_g of 256°C.

We received a sample of a third enyne polysulfone resin (see Figure 6). This resin had 15 percent of enyne portion of the polymer, whereas resin 1814 has 25 percent and BR-2-17 has 35 percent.

We prepared a 24 percent solution of BR-2-22 in dichloromethane. The resin dissolved readily and produced a clear gold solution with a

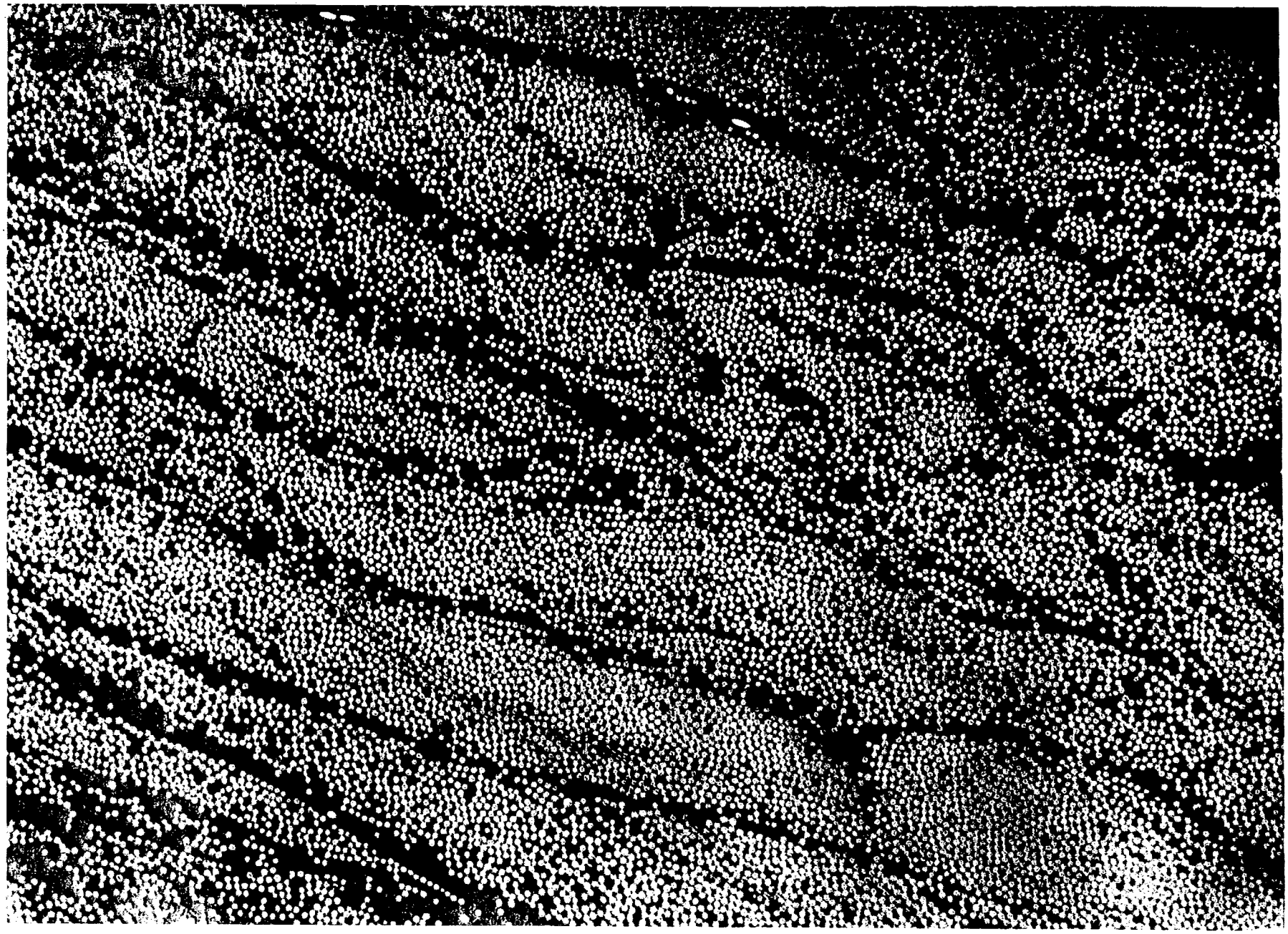


Figure 7 Celion 6000/BR-2-17 Laminate, 100 X

Table 31

A COMPARISON OF THE SHORT-BEAM SHEAR PROPERTIES OF RADEL 5000 AND THE TWO PREVIOUS ENEYNE SULFONE RESINS

Test Temperature (°C)	Aging	Radel 5000 (0%)*		BR-2-17 (15%)*		Resin 1814 (25%)*	
		Shear Strength (MPa)	% Retention	Shear Strength (MPa)	% Retention	Shear Strength (MPa)	% Retention
RT	None	65.5	--	74.05	--	67.6	--
177	None	39.0	60	51.2	69	39.55	59
RT	Skydrol†	65.9	101	74.08	100	66.9	99
177	Skydrol†	35.3	91	51.9	101	38.8	98
RT	MEK‡	26.5	40	--	--	55.9	83
177	MEK‡	23.5	60	--	--	24.8	63

*Denotes the percentage of enyne component.

†Samples were aged in Skydrol at 71°C.

‡Samples were aged in methyl ethyl ketone at room temperature.

viscosity suitable for prepregging. The solution was then prepregged onto unsized Celion 6000 using the conditions developed for BR-2-17. The resulting prepreg was smooth and even, appeared well wet-out, and had no drape and tack at room temperature.

We conducted a TMA study on this prepreg to help determine cure conditions. The results of this study are given in Table 32.

Based on the TMA and DSC data, we laid up a 1.9 x 3.8 cm, $[0]_9$ laminate. The laminate was vacuum-bagged* and cured as follows:

- Apply full vacuum
- Place assembly in 200°C press
- Apply 6.9 MPa
- Hold 3 hrs
- Heat to 350°C
- Hold 2-1/2 hrs
- Cool slowly under vacuum and pressure.

Table 32

A TMA STUDY OF BR-2-22/CELION 6000 PREPREG

Conditions	T_g	Remarks
A DSC of BR-2-22	200°C	
Sample heated 1-1/3 hr at 200°C	168°C	2.7% weight loss
+ 1-1/2 hr at 200°C	197°C	+0.8% weight loss; total weight loss = 6.5%
+ 1 hr at 300°C	252°C	+0.71% weight loss; total weight loss = 7.2%
+ 1 hr at 300°C	255°C	Very brittle
+ 1 hr at 350°C	288°C	Signs of decomposition

The resulting laminate had a good appearance and a clear C scan. It lost 12 percent volatiles during cure, and there was no flow into the bleeder, although some flow was observed from the ends of fibers.

Table 33

A COMPARISON OF THE SHORT-BEAM SHEAR PROPERTIES OF RADEL 5000 AND THREE ENEYNE SULFONE RESINS

Test Temperature (°C)	Aging	Radel 5000 (0%)*		BR-2-17 (15%)*		Resin 1814 (25%)*		BR-2-22 (35%)*	
		Shear Strength (MPa)	% Retention	Shear Strength (MPa)	% Retention	Shear Strength (MPa)	% Retention	Shear Strength (MPa)	% Retention
RT	None	65.5	--	74.05	--	67.6	--	83.2	--
177	None	39.0	60	51.2	69	39.55	59	53.1	64
RT	Skydrol†	65.9	101	74.08	100	66.9	99	83.1	100
177	Skydrol†	35.3	91	51.9	101	38.8	98	56.5	106
RT	MEK‡	26.5	40	--	--	55.9	83		
177	MEK‡	23.5	60	--	--	24.8	63		

*Denotes the percentage of enyne component.

†Samples were aged in Skydrol at 71°C.

‡Samples were aged in methyl ethyl ketone at room temperature.

The laminate had a density of 1.50 g/cc and a resin content of 42 percent. Optical microscopy of a cross section indicated that the laminate was well-consolidated (Figure 8). The average room temperature short-beam shear strength was 67.9 MPa.

We then proceeded to make additional BR-2-22 prepreg and fabricate a final, 4.4 x 5 cm $[0]_8$, laminate using the parameters already developed for this resin. The final BR-2-22 laminate gave a clear C-scan. The density was 1.53 g/cc, the resin content was 39.1 percent, and the T_g was 267°C.

The laminate was cut into short-beam shear specimens which were then aged; one-third were aged under ambient conditions, one-third in Skydrol at 71°C, and one-third in methyl ethyl ketone (MEK) at room temperature.

Ambient-aged specimens of the final BR-2-22/Celion 6000 laminate were tested at 177°C and produced an average short beam shear strength of 53.1 MPa (see Table 33).

Specimens aged in Skydrol at 71°C gained an average of 0.3 weight percent and dimensions changed by + 0.08 percent. Room temperature short beam shear values averaged 83.1 MPa and at 177°C they averaged 56.5 MPa (see Table 33).

The aging in MEK is not yet complete after 1000 hours of aging. The percentage weight gain is increasing linearly with respect to the square root of time. The specimens are maintaining their integrity. Aging will continue for an additional 30 days or until the pseudosaturation point is reached, whatever comes first. Evidently, MEK resistance is still below desired levels, since solvent pickup is continuing.

Figure 8 Celion 6000/BR-2122 Laminate, 100 X

IV CONCLUSIONS AND RECOMMENDATIONS

A. Polyimide Films

In general, the experimental 5- and 6-member ring system proved quite difficult to work with. Processing windows proved to be very small. The processing was further complicated by surface tension, viscosity, and phase change phenomena.

Satisfactory films were made with some difficulty; since they were prepared for AFML evaluation, no conclusions or recommendations can be made from the work at SRI.

B. RPS/P1700 as Matrix Resin

Our work with the various RPS/P1700 blends was successful and demonstrated the concept of reactive plasticizers. A full range of blends was investigated; we found that solvent resistance, Tg, and other properties could be precisely tailored by use of the appropriate blend of RPS/P1700.

We believe the concept should be extended to more difficult to process high temperature thermoplastic such as polyphenylsulfone, PPQ, and thermoplastic polyimides, where there is significant potential payoff in the development of a tough, processable, high temperature resin for composite and adhesive applications.

C. Enyne Polysulfone as a Matrix Resin

The concept of a linear polyphenyl sulfone containing a reactive enyne structure was successfully demonstrated in our work. High quality panels were fabricated from resins containing several levels of enyne. Composites with matrices containing as little as 15 percent enyne structure showed excellent Skydrol environmental resistance when compared with commercial polyphenyl sulfone resins.

On the other hand, enyne levels as high as 35 percent failed to provide satisfactory resistance to MEK aging, although their performance was significantly better than that of commercial polyphenyl sulfone resin. It appears that the approach is technically sound. We recommend that other polymers be investigated to exploit the potential payoff in IMC resin systems.

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